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THE OXIDATION POTENTIAL OF THE LEAD DIOXIDE ELECTRODE IN PERCHEORIC ACID SOLUTION

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A great amount of work has been done on the lead dioxide electrode by those who used lead dioxide storage cell plates and sulfuric acid. A few used nitric acid. The concentrations were almost always high. Abegg,[1] based on these early results, gave the value +1.44 for the "normal potential." Glasstone,[2] the only more recent worker, concluded that "a mean value of 1.75 volts at 25° is indicated." The minimum concentration of acid used by Gladstone was 0.487 molar. Gerke[3] apparently considered none of the data suitable for the calculation of a value to include in his summary.

In our work the cell arrangement was

$$\text{Pt}, PbO_2 \mid Pb(ClO_4)_2, HClO_4 \mid \text{Hz, Pt}$$

The reaction of the cell is

$$PbO_2 + 2H^+ + H_2(g) = Pb^{++} + 2H_2O(l)$$

The free energy change for this reaction is

$$AF = -NFE, = -NFE_c - RT \ln \frac{a_{Pb^{++}} \times a_{H_2O}}{a^2_{H^+}}$$

in which E_c is the voltage after correcting for the pressure of the hydrogen and it is assumed that the activity of the PbO_2 is unity. The oxidation potential at unit activity is

$$E_0 = E_c + \frac{RT}{2F} \ln \frac{a_{Pb^{++}} \times a_{H_2O}}{a^2_{H^+}}$$

$$= E_c + \frac{RT}{2F} \ln \frac{\gamma m_{Pb(ClO_4)_2} \times a_{H_2O}}{(\gamma m_{HClO_4})^2}$$

In the first series of measurements (Table I) the concentrations of the perchloric acid and lead perchlorate were equimolecular and the same throughout the cell, then

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[1] Abegg, Auerbach and Luther, "Messungen electromotorischer Krafte galvanischer Ketten," 207, 70–77, 168–169 (1911).

[2] Glasstone, *J. Chem. Soc.*, 121, 1469–1480 (1922).

[3] Gerke, *Chemical Reviews*, 1, 390–391 (1924).

$$E_0 = E_c - \frac{RT}{2F} \ln m + \frac{RT}{2F} \ln \frac{\gamma_{\mathrm{Pb(ClO_4)_2}} \times a_{\mathrm{H_2O}}}{\gamma^2_{\mathrm{HClO_4}}}$$

from the observed values $E' = E_c - RT/2F \ln m$ was calculated and extrapolated to zero concentration. If we assume that

$$\frac{RT}{2F} \ln \frac{\gamma_{\mathrm{Pb(ClO_4)_2}} \times a_{\mathrm{H_2O}}}{\gamma^2_{\mathrm{HClO_4}}} \doteq 0$$

on dilution, this extrapolated value is E_c.

In the second series (Table II) the concentration of the perchloric acid was kept constant throughout the cell and the concentration of the lead perchlorate was varied in the lead dioxide electrode. Since the concentrations of the lead perchlorate were relatively low, the liquid junction potentials were negligible.[4] The oxidation potential, E_0, was calculated assuming that the activity of perchloric acid[5] is the same as that of hydrochloric acid as determined by Randall and Young,[6] that the activity of water was unity and that the activity of the lead perchlorate was the same as that of barium chloride.[7] This second series was made as a check on the first. The first is the basis for the determination of the oxidation potential.

Experimental Part

Doubly distilled water was used in the preparation of all solutions. Perchloric acid was obtained by dilution of the 60% C. P. acid and standardized against sodium carbonate. Lead perchlorate was prepared by the action of this acid on purified lead carbonate from C. P. lead nitrate. The concentration of this solution was determined with dichromate according to the method of Brown and Moss.[8]

Two hydrogen electrode vessels of the Ostwald type and triplicate or quadruplicate hydrogen electrodes prepared by a modification of the method of Ellis[9] were used in each measurement. Hydrogen was prepared by electrolysis of 15% sodium hydroxide and passed successively through glass wool, 20% perchloric acid, M perchloric acid, and a washer containing the electrode solution. The purity of this hydrogen was established[10] by checking an electrode for which it was used against another which obtained hydrogen from the action of C. P. hydrochloric acid on C. P. zinc. It is known that a solution of lead acetate has a depressing effect on the hydrogen electrode and on the adsorption of hydrogen by

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[4] Linhart, THIS JOURNAL, 38, 2356 (1916).

[5] Schumann, *ibid.*, 46, 58 (1924).

[6] Randall and Young, *ibid.*, 50, 995 (1928).

[7] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 362.

[8] Unpublished material.

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

[10] Smith, *ibid.*, 27, 1287 (1905).

catalytic platinum. Denham and Allmand[11] and Maxted[12] showed that the amount of hydtogen adsorbed varied with the concentration of Pb^{++} ion. In our case it was discovered that hydrogen electrodes in 0.5 M perchloric acid and 0.5 M lead perchlorate did not show a definite equilibrium value, but fluctuated within a range of five millivolts, the value depending on the length of time hydrogen was furnished to the electrode. The same fluctuation occurred in the measurement employing 0.25 *M* lead perchlorate but to a less degree. At 0.1 M lead perchlorate concentration duplicate hydrogen electrodes checked within a maximum of 0.3 of a millivolt. In order to obtain further proof that the effect of lead perchlorate on the hydrogen electrode became negligible at 0.01 M or lower concentration of lead perchlorate duplicate hydrogen electrodes were set up one containing 0.01 M perchloric acid, and the other 0.01 M perchloric acid and approximately 0.01 M lead perchlorate. The potential difference was constant and of the order of 0.75 millivolt, no correction being made for ionic strength and consequent difference in activity of $H+$. In order to make this activity difference negligible, the observations of potential were made with quadruplicate hydrogen electrodes, two in 0.25 M perchloric acid and two in 0.25 M perchloric acid and 0.01 M lead perchlorate solutions and although those in the solution containing lead perchlorate required a longer time to attain equilibrium, the maximum variation was 0.4 millivolt. This is less than the variation in the lead dioxide electrode and consequently would not introduce sufficient error to make it advisable to discard the method as unsuitable if the average value of triplicate[13] or quadruplicate hydrogen electrodes be employed as the reference electrode value, as was done in our case, and taking into consideration the fact that the variation caused by lead perchlorate decreases as the concentration of lead ion becomes smaller.

Electrolytic lead dioxide was deposited on platinized platinum which had been treated with a blast lamp flame to give a rough surface, by electrolysis of basic lead perchlorate or lead nitrate, nitric acid solutions. The best results were obtained by electrolysis of solutions containing 0.1 to 0.5% lead nitrate and 1.5 to 2.5 N in nitric acid. In every case the first electrode plated of a series failed to attain a stable value and the lead dioxide did not adhere very well to the platinum. Electrodes plated with a current density of 0.01 to 0.03 amps./cm.^{2} and a potential drop of 2.2 volts for twenty minutes usually attained a stable value in three to five days and remained constant from three to ten days or longer and then decreased in potential either[12] at a slow uniform rate or abruptly at first and then very slowly. The following are representative:

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[11] Denham and Allmand, **J.** *Chem. Soc.,* **93,** 424 **(1908).**

[12] Maxted, ibid., 117, 1501 (1920).

[13] Glasstone, ibid., 121, 1456 **(1922).**

0.35 M $HClO_4$ and 0.01 M $Pb(ClO_4)_2$			0.001 M $HClO_4$ and $PbClO_4$	
5/ 7/28	set up	1.50369	4/16/28	Set up
5/12/28		1.50175*	4/17/28	1.37904*
5/21/28		1.50133*	4/18/28	1.37604*
5/28/28		1.49790	4/21/28	1.37621"
5/29/28		1.49649	4/24/28	1.37197

The values within the range represented by the starred values were used. The values given in the table are the average of five or six such values which checked within the limits given there.

Glasstone[13] also investigated dioxide prepared in the above manner and suggested that the presence of a trace of higher oxide, possibly PbO_3, was the cause of the high initial value. However, since the best results were obtained by electrolysis of solutions containing small amounts of lead under conditions at which Smith[10] and also A. Fischer and Vossen[14] found that the electrolytic deposit from lead nitrate acid solutions approached and ultimately attained the formula PbO_2 with decreasing lead content and since no one has been able to demonstrate the presence of high oxides in the electrolytic lead dioxide deposit[15] we concluded that the high initial values are due to an excess of energy stored in physical strains such as observed by Nielsen[16] for electrolytically deposited copper.

The decrease in potential following the period of stability is in all probability due to the slow formation of Pb^{++}, which is to be expected due to the value of the oxidation potential of lead dioxide in relation to that for the oxygen electrode. The period of stability varied directly with the length of time used to plate the electrode. After various lengths of time the lead dioxide lost its property of adhering to roughened platinum and in several cases the formation of reddish brown spots in the deposit was observed. One electrode plated for eight hours at approximately 0.003 amp./cm.^{2} was used in four measurements and each time attained a constant value after three or four days which checked that of freshly prepared electrodes. In all, this electrode was used for two and one-half months and was lost by an accident.

Cumming,[17] who also used lead dioxide deposited on platinum from lead nitrate nitric acid solutions, saturated his electrolytic solution with solid lead dioxide before plating in order to obtain an adhering deposit and good results. Cumming also reported that an electrolytic lead dioxide electrode first gave a high initial value, fell to one that remained constant for various lengths of time and then slowly dropped off.

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[14] Fischer and Schleicher, "Electranalytische Schnellmethoden," zweite Auflage, 1926, p. 243.

[15] (a) MacInnes and Townsend, *J. Ind. Eng. Chem.*, 14, 120 (1922); (b) MacInnes, Adler and Joubert, *Trans. Am. Electrochem. Soc.*, 37, 641 (1920).

[16] Nielsen, THIS JOURNAL, 49, 2423 (1927).

[17] Cumming, *Z. Electrochem.*, 13, 19 (1907).

Chemical lead dioxide was prepared by adding bleaching powder, sodium hypochlorite and bromine water solutions to boiling solutions of lead acetate, washing repeatedly with water, hot dilute nitric acid, again with water and drying at 80 to 110°. The four best grades of lead dioxide obtainable were repurified by boiling with 10% sodium hydroxide and then digested with dilute nitric acid, washed and dried. All this work was done and the electrodes were set up by inserting a smooth platinum foil in a quantity of lead dioxide in the bottom of the electrode vessel in an atmosphere free from hydrogen. Only the repurified dioxide and that prepared with bleaching powder gave constant potential values and those only in solutions containing 0.025 *M* or higher concentrations of lead perchlorate, even after twenty-four hours rotation and repeated purification with dilute nitric acid or perchloric acid to remove divalent lead, which was tested for by shaking up lead dioxide with nitric acid of perchloric acid decanting, adjusting the acid concentration and adding potassium chromate. Negative tests were obtained immediately after purification. However, the lead dioxide gave a test for Pb^{++} upon standing dry in stoppered amber bottles in the dark for a week. From the energy relations involved it would be expected that lead dioxide is unstable in neutral or acid solution. However, it would not be expected to decompose when dry in the dark and protected from hydrogen. The potentials of the repurified lead dioxides were initially high or low depending on whether they were prepared by chemical oxidation or electrolytic methods. The equilibrium potential value of the chemical lead dioxide remained constant indefinitely and agreed within a millivolt or two with the average stable value of a number of electrolytic lead dioxide electrodes.[13,15b]

The experimental half cell consisted of a pyrex test-tube with a sealed-in side arm and closed by a one-holed rubber stopper through which a glass tube with a platinum foil sealed in the lower end was inserted. Contact was made to the potentiometer by filling the tube with mercury and inserting the potentiometer lead.

Wquid contact was established between the electrodes by allowing the side arms to dip in a vessel which contained the same solution as the electrodes in the first series of measurements and in the second series contained the same concentration of perchloric acid as the hydrogen electrode. This intermediate vessel was protected from evaporation by a layer of purified paraffin, which was found not to affect the measured values in any way.

Temperature was maintained constant at 25 ± 0.03°. The potential differences were measured with a Leeds and Northrup Type K potentiometer, and a new Weston Standard cell calibrated by the U. S. Bureau of Standards.

In the following tables E_c is the average first stable value of five or six electrolytic lead dioxide electrodes.

TABLE I

EXPERIMENTAL DATA

Mole $HClO_4$ = mole $Pb(ClO_4)_2$	E_c, mv.	E'
0.1	1.432 ± 3	1.461
.025	1.417 ± 3	1.464
.1	1.407 ± 3	1.466
.0025	1.389 ± 2	1.467
.001	1.378 ± 2	1.467
E_0 by extrapolation of E'		1.467

TABLE II

EXPERIMENTAL DATA

$HClO_4$, mole (per 1000 g. of H_2O)	$Pb(ClO_4)_2$, mole (per 1000 g. of H_2O)	E_c	E_0
0.25	0.01	1.501	1.475
.25	.001	1.523.	1.467
.25	.0001	1.549	1.464
		E_0 average	1.469

Summary

1. The possible sources of error in the previous work on the lead dioxide electrode have been discussed.

2. The work of former investigators who found the first stable value of electrolytically prepared lead dioxide to agree within one or two millivolts with the potential of that obtained from chemical sources has been checked.

3. An attempt has been made to explain the high initial value and the final drop in potential of electrolytic lead dioxide. The factors involved in lengthening the stable period of this lead have also been studied.

4. The effect of lead perchlorate on the hydrogen electrode has been investigated and found to be proportional to the Pb^{++} concentration.

5. The standard oxidation potential of Pb^{++}–PbO_2 in molal H^+ has been measured by two methods and found to be 1.467 ± 0.003 volts.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 205]

SOME OF THE THERMODYNAMIC PROPERTIES OF AMMONIA. I. THE COMPRESSIBILITY OF AND AN EQUATION OF STATE FOR GASEOUS AMMONIA. THE VAPOR PRESSURE OF LIQUID AMMONIA

BY JAMES A. BEATTIE AND CHARLES K. LAWRENCE

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1. Introduction

The compressibility of gaseous ammonia is of interest because the curvature of the isometries is greater than for any other gas, except steam, for which there is a considerable body of data. The earlier measurements either do not extend over a very wide range, or the volumes were uncertain. Roth[1] studied the pressure–volume–temperature behavior of ammonia from 30 to 180°, but his volumes were not definitely determined;

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[1] Roth, *Wied.* **Ann., 11, 1 (1880).**

Brownlee, Babcock and Keyes[2] measured the compressibility for two isotherms, and determined the values of the constants of the Keyes equation of state for ammonia from the existing data, and Keyes[3] presented data for five isometries extending from 39 to 55 cc. per gram and from 60 to 164°. Holst[4] measured the pressure at several volumes and temperatures from 24 to 100° and from 3 to 21 atmospheres; and Bridgman[5] investigated the high pressure field from 1000 to 12,000 atmospheres for the temperature 30°.

Meyers and Jessup[6] of the Bureau of Standards made a study of the compressibility of ammonia in the low pressure region. The measurements were made by the isometric method and extended from 85.5 to 1300 cc. per gram and from -35 to $+300°$. -These data will be discussed in a later section.

In the present paper there is presented a series of pressure–volume–temperature measurements on gaseous ammonia, extending from 20 to 95 cc. per gram and from 75 to 325°. These data and those of Meyers and Jessup are correlated by means of an equation of state.

The vapor pressure of liquid ammonia has been measured by Cragoe, Meyers and Taylor[7] of the Bureau of Standards from -80 to $+70°$; and by Keyes and Brownlee[8] from the boiling point to the critical point. The data of the authors, which extend from 30 to 132°, agree very well with those of the Bureau of Standards and fairly well with the values of Keyes and Brownlee.

2. The Experimental Method

All of the measurements were made by the isometric method, the details[9] of which have been described in a paper on the compressibility of gaseous ethyl ether. Some modifications in the apparatus however deserve to be mentioned.

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[2] (a) Brownlee, Babcock and Keyes, *Proceedings of the Third International Congress Refrig.*, Vol. II, p. 189 (1913); also Keyes, *Am. Soc. Refrigerating Eng. J.*, 1, 9 (1914); (b) Keyes and Brownlee, "The Thermodynamic Properties of Ammonia," John Wiley and Sons, Inc., New York, 1916, p. 20.

[3] Keyes, *Am. Soc. Refrigerating Eng. J.*, 7, 371 (1921).

[4] Holst, *Bull. Assoc. International Froid.*, 6, 48 (1915).

[5] Bridgman, *Proc. Nat. Acad. Sci.*, 9, 370 (1923).

[6] Meyers and Jessup, *Refrig. Eng.*, 11, 345 (1925). The compressibility of liquid ammonia between saturation and 50 atmospheres is given in Circular of Bureau of Standards, No. 142, Table 4.

[7] Cragoe, Meyers and Taylor, THIS JOURNAL, 42, 206 (1920); *Scientific Papers of the Bureau of Standards*, 16, 1 (1920).

[8] Keyes and Brownlee, THIS JOURNAL, 40, 25 (1918). See also Keyes, "International Critical Tables," National Research Council, McGraw-Hill Book Co., 1928, Vol. III, p. 234.

[9] Beattie, THIS JOURNAL, 46, 342 (1924).

The Thermostat.—A larger thermostat was used in the present investigation. It was a liquid bath 36 cm. in diameter and 75 cm. deep, mineral seal oil being used at the lower temperatures and heavy cylinder oil at the higher temperatures. The stirring was accomplished by three sets of propellers each enclosed in a steel tube and geared together. One of these stirrer casings had a larger tube welded around its lower end, thus forming an annular space about 0.5 cm. in width and 20 cm. long which contained about 200 cc. of mercury. The expansion and contraction of this mercury operated a relay which turned on and off the electric current in the three internal heaters, one of which was placed on the top of each stirrer tube. Sufficient current was constantly passed through external heaters to raise the temperature of the bath to within about 2° of the desired value. The temperature regulation was ±0.001° over the entire range from 75 to 325°.

The temperatures were measured by a four-lead potential type platinum thermometer calibrated as described in the earlier paper. All temperatures are on the platinum scale.

The Pressure Gage.—The gage had been modified somewhat[10] and was calibrated against the vapor pressure of carbon dioxide at 0°, this value being taken as 34.401 atmospheres.[11]

The volume measuring device and piezometer were the same as those used in the measurements on ethyl ether but the connecting and riser block was simplified so that only one steel stopcock was used in the entire volume measuring system.

3. Filling the Piezometer

A commercial sample of liquid ammonia was allowed to stand in a vessel containing sodium for about three months, the gas phase being removed from time to time by "blowing off." The method of filling the glass piezometer was the same as that used for ethyl ether. The ammonia was distilled eight times, the first and last portion being rejected each time, and the ammonia frozen while the entire system was evacuated after each distillation. It was finally distilled into the glass bomb, which had been evacuated for six days, first at 400° and later at 350°. The ammonia was then frozen by liquid air and the bomb sealed. The amount of ammonia used was determined by weighing against a counterpoise which had approximately the same outside and inside volume as the bomb. The counterpoise was evacuated when weighing the loaded bomb so that the buoyancy correction was small.

After each loading the vapor pressure of ammonia was measured at 30°. No increase in vapor pressure was observed even when the gas space was reduced to 0.1 or 0.2 cc. In one case after the gas phase had been completely collapsed, it did not re-form for some minutes even though the external pressure was reduced to less than one atmosphere. After each series of measurements the vapor pressure was determined again but no evidence of a decomposition of the ammonia could be detected.

The method of calculation of the results has been fully described elsewhere.[9] All volumes are relative to those of mercury, whose density at one atmosphere and various temperatures was calculated from the Callendar and Moss equation.[12] The temperature coefficient of the compressibility of mercury used was

$$\frac{1}{V_0}\frac{d}{dp}\left(\frac{dV}{dT}\right) = 5 \times 10^{-9} \text{ atmospheres}^{-1} \text{ degrees centigrade}^{-1}$$

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[10] See Keyes and Dewey, *J. Opt. Soc. Am.*, 14, 491 (1927).

[11] O. C. Bridgeman, This Journal, 49, 1174 (1927).

[12] Callendar and Moss, *Phil. Trans. Roy. Soc.*, 211, 1 (1912).

The measured pressures were corrected for the vapor pressure of mercury. For this purpose the saturated vapor pressures of Smith and Menzies[13] were used and a correction applied by the Poynting relation for the effect of pressure on vapor pressure.

Two runs were made: one extending from 95 to 35 cc. per gram, and the other from 40 cc. per gram to higher densities. In this latter run a leak developed at the higher pressures, so that the measurements at densities higher than 20 cc. per gram are too uncertain to include in the data, and the pressures of the 20 cc. per gram isometric may be in error by several tenths of an atmosphere.

4. Discussion of the Experimental Data

The data are given in Table II, in which the measurements of Meyers and Jessup are also included. Since these two sets of results cover different density ranges, they can only be compared by means of some smoothing function, and for this correlation the Beattie–Bridgeman equation of state[14] is used.

The method of determining the values of the constants from the experimental data has been given elsewhere.[14b] In Table I are given the form of the equation of state and the values of the constants in several sets of units. In the evaluation of the constants most weight was given to the authors' data, as they are at the higher densities. The comparison of the observed and calculated pressure is given in Table II, from which it can be seen that the average deviation of the equation from the measured values is 0.037 atmosphere or 0.077% for the author's data, and 0.012 atmosphere or 0.155% for Meyers and Jessup's data.

TABLE I

VALUES OF THE CONSTANTS OF THE BEATTIE–BRIDGEMAN EQUATION OF STATE FOR AMMONIA

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

$$A = A_0(1 - a/V) \qquad B = B_0(1 - b/V) \qquad \epsilon = c/VT^3$$

R	A_0	a	B_0	b	c	Mol. wt.
Units: atmospheres; cc. per gram; °C. (T°K. = t°C. + 273.13)						
4.81824	8250	10	2.005	11.222	280×10^6	17.0311
Units: atmospheres; liters per mole; °C.						
0.08206	2.3930	0.17031	0.03415	0.19112	476.87×10^4	17.0311
Units: atmospheres; $V = 1$ at 0°C. and 1 atm.; °C. (Amagat units)						
3.71274×10^{-3}	4.8986×10^{-3}	7.706×10^{-3}	1.5451×10^{-3}	8.647×10^{-3}	215.76×10^3	17.0311

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[13] Smith and Menzies, THIS JOURNAL, 32, 1434 (1910).

[14] Beattie and Bridgeman, (a) *ibid.*, 49, 1665 (1927); *ibid.*, 50, 3133 (1928); **(b)** *Proc. Am. Acad. Arts and Sci.*, **63**, 229 (1928).

TABLE II

COMPARISON OF THE PRESSURES CALCULATED FROM THE EQUATION OF STATE WITH THE OBSERVED PRESSURES

For each temperature the first line gives the observed pressure and the second line gives the observed minus the calculated pressure. The equation used for the calculated pressures is given in Table I.

A. Data of Beattie and Lawrence

Volume, cc./g. Temp., °C.		95	90	80	70	60	50	45	40	35	30	25	20
		Pressures in atmospheres											
325	Obs.	29.59	31.22	35.04	39.90	46.34	55.24	61.11	68.36	77.59	89.69	106.25	130.40
	Obs.−calcd.	−0.07	−0.05	−0.03	−0.03	−0.01	0.00	0.02	0.02	0.05	0.08	0.10	0.12
300	Obs.	28.29	29.84	33.45	38.08	44.18	52.62	58.16	65.03	73.68	85.09	100.61	123.10
	Obs.−calcd.	−0.04	−0.02	−0.03	−0.02	−0.01	0.01	0.01	0.03	0.00	0.05	0.05	−0.02
275	Obs.	26.98	28.44	31.87	36.25	42.00	49.96	55.18	61.62	69.77	80.45	94.88	115.67
	Obs.−calcd.	−0.01	−0.01	−0.01	−0.01	0.02	−0.01	−0.01	−0.01	−0.01	0.04	−0.01	−0.16
250	Obs.	25.64	27.01	30.27	34.39	39.83	47.33	52.22	58.26	65.86	75.74	89.11	108.18
	Obs.−calcd.	−0.01	−0.02	0.00	−0.01	0.00	0.02	0.02	0.03	0.03	0.02	−0.01	−0.21
225	Obs.	24.30	25.59	28.64	32.54	37.64	44.63	49.20	54.81	61.85	70.97	83.21	100.51
	Obs.−calcd.	0.00	−0.01	−0.01	0.01	0.01	0.02	0.02	0.03	0.03	0.02	−0.03	−0.27
200	Obs.	22.93	24.15	27.01	30.64	35.40	41.89	46.12	51.29	57.74	66.05	77.13	92.57
	Obs.−calcd.	−0.02	−0.01	−0.01	−0.01	0.00	0.00	0.01	0.01	−0.01	−0.03	−0.10	−0.39
175	Obs.	21.56	22.70	25.36	28.74	33.14	39.13	43.01	47.73	53.61	61.11	70.98	84.54
	Obs.−calcd.	−0.02	−0.01	−0.01	0.00	0.00	0.01	0.02	0.02	0.03	0.01	−0.06	−0.32
150	Obs.	20.18	21.23	23.70	26.81	30.86	36.33	39.85	44.11	49.36	56.01	64.65	76.24
	Obs.−calcd.	−0.01	−0.01	0.00	0.00	0.02	0.03	0.04	0.05	0.04	0.04	0.00	−0.20
125	Obs.	18.78	19.75	22.00	24.85	28.51	33.44	36.59	40.36	44.99	50.74	58.06	67.56
	Obs.−calcd.	−0.01	0.00	−0.01	0.01	0.01	0.03	0.05	0.05	0.08	0.09	0.08	−0.05
100	Obs.	17.36	18.24	20.28	22.84	26.12	30.47	33.21	36.47	40.41	45.19	51.09	58.28
	Obs.−calcd.	−0.01	0.00	0.00	0.01	0.02	0.03	0.04	0.04	0.07	0.08	0.11	0.04
75	Obs.	15.90	16.68	18.50	20.76	23.61	27.34	29.65	32.35	35.52			
	Obs.−calcd.	−0.01	0.00	−0.01	−0.01	−0.02	−0.02	−0.02	−0.02	−0.02			
50	Obs.	14.37	15.05	16.62	18.54								
	Obs.−calcd.	−0.05	−0.06	−0.07	−0.09								
Av. dev. (atm.)		0.022	0.017	0.016	0.018	0.011	0.016	0.024	0.028	0.034	0.046	0.055	0.178
Av. % dev.		0.101	0.076	0.070	0.073	0.035	0.045	0.059	0.060	0.067	0.076	0.077	0.191

Total average deviation (atm.) 0.037

Total average % deviation 0.077

TABLE II (*Concluded*)

B. Data of Meyers and Jessup

Volume, cc./g.		1300	500	300	200	150	115	85.5
Temp., °C.		Pressures in atmospheres						
300	Obs.			9.126	13.631	18.101	23.497	
	Obs. − calcd.			−0.004	−0.008	−0.010	−0.009	
250	Obs.		5.007	8.308	12.395	16.439	21.305	28.378
	Obs. − calcd.		−0.002	−0.004	−0.007	−0.009	−0.010	−0.018
200	Obs.	1.747	4.519	7.489	11.153	14.766	19.098	25.361
	Obs. − calcd.	−0.001	−0.002	−0.002	−0 005	−0.006	−0.004	−0 007
150	Obs.	1.561	4.030	6.664	9.902	13.075	16 858	22 285
	Obs. − calcd.	0.000	−0.001	−0.003	−0.002	−0.004	−0.001	0.003
100	Obs.	1.374	3.537	5.832	8.632	11.352	14.567	19.109
	Obs. − calcd.	−0.001	−0.002	−0.002	−0.002	−0.004	0.001	0.003
50	Obs.	1.187	3.039	4.985	7.327	9.567	12.162	15.722
	Obs. − calcd.	0.000	−0.003	−0.005	−0.009	−0.017	−0.027	−0.058
35	Obs.						11.391	
	Obs. − calcd.						−0.061	
30	Obs.					8.812	11.129	
	Obs. − calcd.					−0.043	−0.074	
25	Obs.	1.092	2.786	4.549	6.645	8.618		
	Obs. − calcd.	−0.001	−0.005	−0.012	−0.026	−0.052		
15	Obs.				6.361			
	Obs. − calcd.				−0.040			
10	Obs.			4.279				
	Obs. − calcd.			−0.021				
5	Obs.			4.188				
	Obs. − calcd.			−0.024				
0	Obs.	0.997	2.528					
	Obs. − calcd.	−0.001	−0.009					
−10	Obs.		2.421					
	Obs. − calcd.		−0.014					
−20	Obs.	0.921						
	Obs. − calcd.	−0.001						
−30	Obs.	0.882						
	Obs. − calcd.	−0.002						
−35	Obs.	.865						
	Obs. − calcd.	.000						
Av. dev. (atm.)		.001	0.005	0.009	0.012	0.018	0.023	0.018
Av. % dev.		.073	.173	.180	.168	.186	.194	.098
Total average deviation (atm.)					0.012			
Total average % deviation					.155			

The pressures of Meyers and Jessup are all less than those calculated from the equation of state; but it should be noted that in the low pressure region the authors' measured pressures also tend to be less then the calculated values. It is quite evident from the results given in Table II that the general over-all difference between the two sets of data is less than 0.1%. There is, however, a slight difference in the trends of the two sets of measurements which is evident when the A and B functions are plotted against the density. Hence an equation was passed through the Bureau of Standards data alone. The values of the constants and a comparison of the observed and calculated pressures are given in Table III. The average deviation is 0.004 atmosphere or 0.043%. The great difference in the values of the constants for these data may be due either to the fact that the Bureau of Standards measurements are at low pressures where a very slight difference in trend causes a large change in the values of the constants or to the failure of the equation of state to represent the data near saturation within the experimental error, when the constants are determined from measurements at higher temperatures and pressures. It is probable that both of these factors enter into the present case, but it should be emphasized that the authors' data and those of Meyers and Jessup are in excellent agreement, and that the equation of state has reproduced these data very well.

TABLE III

COMPARISON OF THE PRESSURES CALCULATED FROM THE SPECIAL EQUATION OF STATE FOR THE DATA OF MEYERS AND JESSUP WITH THE OBSERVED PRESSURES

The calculated pressures were computed with the values of the constants given below, which were obtained from a consideration of the data of Meyers and Jessup *alone*. The values of the constants (see Table I for the form of the equation) in units of cc. per gram, atmospheres, °C. (T°K. = t°C. + 273.13) are

R	A_0	a	B_0	b	c
4.81824	3000	51.5	0.45	131	360×10^6

The observed pressures are given in Table IIB

Volume, cc./g.	1300	500	300	200	150	115	85.5
Av. dev. (atm.)	0.000	0.001	0.002	0.004	0.005	0.009	0.007
Av. % dev.	.032	.046	.047	.045	.040	.059	.032

Total average deviation (atm.) 0.004

Total average % deviation .043

5. Weight of a Normal Liter of Ammonia

The weight of a liter of a gas at 0° and one atmosphere, usually called the weight of a normal liter, can be calculated from an equation of state and the molecular weight. The weights of a normal liter of several gases[15] have been evaluated by means of the Beattie–Bridgeman equation of state and agree well with the experimental values. By use of the same method the weight of a normal liter of ammonia was computed using the molecular weight 17.0311 and the comparison with the observed values is given in Table IV. The experimental values are those selected by Blanchard and Pickering,[16] who make no attempt to explain the difference between the weight obtained at the Bureau of Standards, which is the result of two different investigators, and those of other careful observers, which

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[15] Beattie and Bridgeman, THIS JOURNAL, 50, 3151 (1928).

[16] Blanchard and Pickering, *Scientific Papers of the Bureau of Standards, 21,* 141 (1926).

are all very close to 0.7708. The equation based on the authors' determinations of the compressibility of ammonia leads to the value 0.7706, in good agreement with the earlier data; that based on the data of Meyers and Jessup gives a value of the normal density of 0.7715, agreeing with the Bureau of Standards measured value.

The weight of a normal liter obtained by Keyes[2b] from his equation of state is 0.7699 g.

TABLE IV

WEIGHT OR A NORMAL LITER OF AMMONIA

Source	Grams per liter
Calculated from values of constants of Table I	0.7706
Average of experimental values exclusive of those of Bureau of Standards	.7708
Calculated from value of constants of Table III	.7715
Bureau of Standards experimental value	.7713

6. The Vapor Pressure of Liquid Ammonia

The glass bomb was loaded with about 9 g. of liquid ammonia in the same manner as for a compressibility run. The vapor pressure was measured from 30 to 132°. At each temperature the volume of the vapor space was varied from about 80 cc. to less than 1 cc. Thus at 30° the following values were obtained.

Volume of vapor space (cc.)	76	5	2.4	1.8	0.8	0.2
Vapor pressure (atm.)	11.517	11.514	11.515	11.515	11.516	11.515

These values show that no inert gas was present as there is no increase of the vapor pressure with decrease in volume of the vapor space.

The results are given in Table V, in which are included the measurements made at the Bureau of Standards,[7] and those by Keyes and Brownlee.[8] The agreement with the pressures determined at the Bureau of Standards is better than 0.1%, the authors' pressures being higher, but this difference cannot be explained on the basis of permanent gas in the authors' ammonia since the pressure did not increase with decrease of the vapor volume.

TABLE V

VAPOR PRESSURE OF LIQUID AMMONIA

Temp., °C.	Vapor pressure in atmospheres Beattie and Lawrence	Bureau of Standards	Keyes and Brownlee	Temp. °C.	Vapor pressures in atmospheres Beattie and Lawrence	Keyes and Brownlee
30	11.515	11.512	....	100	61.779	61.816
40	15.343	15.339	....	110	74.83	74.84
50	20.074	20.059	....	120	89.98	89.80
60	25.815	25.797	....	125	98.45	98.08
70	32.717	32.687	....	130	107.6	106.9
80	40.894	....	40.902	131	109.6	108.8
90	50.526	....	50.558	132	111.5	110.6

7. Summary

The compressibility of gaseous ammonia has been determined from 20 to 95 cc. per gram and from 75 to 325°. These data agree with the measurements of Meyers and Jessup, which extend from 85.5 to 1300 cc. per gram to better than 0.1%. The constants of the Beattie–Bridgeman equation of state have been determined from these data and their values are given in Table I. The equation of state reproduces the data of the authors with an average deviation of 0.037 atmosphere, or 0.077% and the data of Meyers and Jessup to 0.012 atmosphere or 0.155%.

An equation was passed through the Meyers and Jessup data alone, which represents them to 0.004 atmosphere, or 0.043%.

The weight of a normal liter of ammonia calculated from the equation based on the authors' work is 0.7706 g. and that calculated from the data of Meyers and Jessup is 0.7715 g. The experimental value determined at the Bureau of Standards is 0.7713 g. and the average of all other careful workers is 0.7708 g.

The vapor pressures of ammonia have been determined from 30 to 132°. They agree very well with the Bureau of Standards values, which extend to 70°, and quite well with those of Keyes and Brownlee above 70°.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF BRITISH COLUMBIA]

THE EFFECT OF TEMPERATURE ON THE MOLECULAR SURFACE ENERGY OF BINARY MIXTURES. I

BY W. F. SEYER AND W. S. PECK

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The surface tension of pure liquids has been a subject of much investigation of late. The molecular surface energy has also received a good deal of attention, though this property has been largely studied from the concentration point of view and little attention has been paid to the effect of temperature on surface energy. It is true that Ramsay and Aston[1] determined the surface tensions of a few binary mixtures over considerable ranges and from the results concluded that in those cases examined the molecular weight of the mixture could be taken as the mean of the values for the two substances, but their work was limited to mixtures somewhat similar in properties. An extensive series of measurements has been carried out by Kremann and Meingast.[2] Unfortunately, the temperature interval over which they measured the surface tension was small and consequently little could be learned from their figures in regard to the effect of temperature on the molecular surface energy of binary mixtures.

An interesting series of solubility relationships is that shown by the

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[1] Ramsay and Aston, *Proc. Roy. Soc. London, 55, 184 (1894).*

[2] Kremann and Meingast, *Monatsh.*, 35, **1323** *(1914).*

solubility of hydrocarbons in liquid sulfur dioxide.[3] In seeking an explanation for the extraordinary solubility of benzene in liquid sulfur dioxide (the liquids are miscible in all proportions), it became desirable to know the surface tensions of various solutions at temperatures lying between their freezing and boiling points. It is reasonable to suppose that in the case of complete miscibility in such chemically divergent liquids as those above, some sort of compound formation ought to exist in their solutions. While the freezing-point curve gave no such indication of chemical combination, yet it was thought that the existence of unstable complexes in solution might not be altogether precluded, and an examination of Eotvos constant, Ke, and its behavior with temperature in solutions of varying concentrations, might show that this was the case. As a result of the work of Jaeger[4] and others, the exact significance of this constant is much in doubt. It has been shown to be dependent upon the nature and size of the molecule. In this respect it is no different from other so-called constants which are connected with the various properties of liquids. Ramsay long ago pointed out that the problem dealing with the molecular weights of liquids in solution is a complex one. Upon mixing and forming a homogeneous phase, the following possibilities present themselves: either one or both of the liquids may become associated; if already associated before mixing, they may become more or even less associated; they may associate one with the other, thereby forming what are usually referred to as solvates. Association should in any case be accompanied by a low value of the Eotvos constant. The breaking down of these complex molecules would then be reflected by an increased value of Ke which should reach a limiting value of 2.12 when all the molecules were in their normal state. A higher value than the theoretical cannot be satisfactorily explained by merely assuming dissociation of the normal molecule, and Walden and Swinne[5] have therefore put forward the suggestion that this can readily be accounted for, if the size of the molecule be taken into consideration. In a similar manner, a high value of the constant in the case of binary mixtures can be explained by the formation of complexes. Additional support of the above explanation would be found if it could be shown that this constant decreased with temperature. It was with this object in view that the following work was done.

Experimental Procedure

The most suitable method for measuring the surface tension of liquid mixtures over an extended range of temperature is the differential capillary rise method as described by Richards, Speyers and Carver.[6]

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[3] Seyer and Hugget, Seyer and Gill, Seyer and Gallaugher, *Trans. Roy. Soc. Canada*, Nos. XVI, XVIII and XIX.

[4] Jaeger, *Z. anorg. allgem. Chem.*, *10*, 1 (1917).

[5] Walden and Swinne, *Z. physik. Chem.*, 82, 290 (1913).

[6] Richards, Speyers and Carver, THIS JOURNAL, 46, 1196 (1924).

This method requires a knowledge of the densities of the liquids, for calculating surface tension, but as this has to be determined in any case before the molecular surface energy can be obtained, it was not considered a serious objection. The pyrex capillary tubes used were found to have a variation in diameter of less than one part in two thousand. Two of these tubes having radii of **0.1125** and **0.0236** cm. were fused together in such a way as to present the appearance of a tuning fork (Fig. **1**) The lower end of this was then sealed into a thick-walled pyrex tube, **2.5** cm. in diameter and **15** cm. in length. **A** second apparatus was made in the same way.

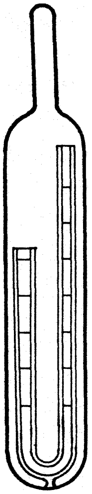
Fig. 1.

A Dewar tube served as a container for the liquids in which the surface tension tubes were to be immersed. **A** number of tubes were examined as regards their optical properties and the one selected as suitable was then tested further in the following manner. **A** surface tension tube was partly filled with water and allowed to come to room temperature. It was suspended above the Dewar tube and while in that position the difference in height of the two menisci was measured by means of a cathetometer reading to **0.05** mm. The tube was next immersed in the bath, which was also at room temperature, and the difference in height again measured through the walls of the Dewar. No difference in the two readings could be detected. Rotating the Dewar tube appeared to make no sensible difference in the cathetometer readings. Nevertheless, the tube was so marked that readings were always taken through the same region.

The next step was to determine the constant of the surface tension tubes. Richards has shown that for both tubes the following equation holds: $S = Khd$, where S is the surface tension, K a constant for the apparatus, h the corrected difference in height and d the density of the liquid minus the density of the vapor. Water was used to determine the value of the constant in the case of Tube **1** and benzene for Tube **2.** These tubes were first thoroughly cleaned with aqua regia, rinsed many times with distilled water and finally water was boiled in them for some time. The tubes were then drained and again rinsed with conductivity water. After several rinsings, Tube **1** about half full of water was boiled under reduced pressure until it was thought that all air had been expelled and then sealed. After the tube had been immersed in the bath for several hours at 20°, the difference in height in the two capillary tubes was measured and found to be **4.875** cm. The correction for curvature as calculated from the known radii of the two tubes amounted to **0.0295,** giving a corrected value of h equal to **4.8435.** Using this and taking the value of the surface tension of water as **72.80** and the density minus the density of the vapor as 0.9982, the constant comes out to be equal to **15.026.** The accuracy of this figure was then further tested by determining the surface tension of benzene at 20°. The corrected difference in height was found to be **2.1875.** Taking the density of benzene minus that of the vapor as **0.8787,** and inserting the above figures in the equation $S = Khd$, the surface tension of benzene is found to be **28.87.** Richards, Speyers and Carver in a series of careful measurements give the value as **28.88.** **A** second tube was then made and its constant determined in a similar manner. Its value was **18.482** and the correction for the menisci **0.0250.**

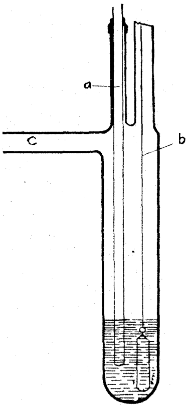

Fig. 2.

The densities were determined by three different methods. Those of the pure sulfur dioxide and of the solutions with benzene below −**10**° were determined by weighing a quartz bulb suspended in the liquid, which was held in a special tube (Fig. 2).

The stem of a platinum resistance thermometer (a) was placed in a limb of the tube, closed at the top with a piece of rubber. The thread for holding the sinker passed through (b). Dry air was gently blown through (c), except when actual weighings were being taken, to prevent any moisture from condensing in the bulb.

The tube itself was placed in a constant-temperature bath. The liquid inside was stirred by moving the sinker up and down. With a bulb having a volume of 8.5095 cc., the surface tension effect on the thread could be disregarded, and by always keeping the bulb the same distance below the surface, no difficulty was experienced in measuring to the fifth decimal place.

The density of pure sulfur dioxide above −15° was measured in a special form of apparatus (Fig. **3).** It was essentially a dilatometer enclosed in a stout glass tube which had been carefully selected with regard to its optical properties. The chief advantages of this form of dilatometer were its compactness and the large range over which it could be used, being limited in fact, solely by the strength of the glass walls. Operation was comparatively simple. After having been evacuated, the tube was filled to one-third of its volume with liquid sulfur dioxide and sealed. Liquid could be caused to run into the inner tube by merely inverting the apparatus and cooling the upper end. When enough liquid had run in, the apparatus was righted and placed in a constant-temperature bath. As soon as equilibrium had been established, the height of the liquid in the capillary tube was read and having previously determined the volume of the bulb up to a certain mark on the capillary, and knowing the radius of the capillary **(10.0282cm.)**, the density of the liquid easily could be calculated.

The temperature of the bath was next raised 10° and the height of *the* capillary read until there was no further rise. The error introduced by the distillation of liquid from the outside tube to the inner one, owing to the difference of temperature when the bath was first warmed, was found to be extremely small and therefore negligible. The length of the capillary was sufficient to cover a range of **20".** When the liquid in the capillary stood at the top the dilatometer was placed in a bath that was 20° higher than the one in which the last measurement had been taken and enough allowed to flow out so that when the temperature was again reduced **20°**, the liquid stood at the bottom of the capillary. Measurements could then be made over another **20"** interval.

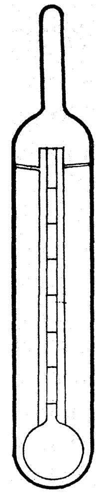

Fig. 3.

While the above method worked admirably for the pure sulfur dioxide liquid, much difficulty was encountered when attempting to measure the densities of the mixtures. This was due entirely to the wide range in boiling points comprising the mixture. The densities of these solutions were, therefore, measured in an ordinary dilatometer, sealed at the top. This, of course, introduced an error owing to the expansion of the glass, caused by the vapor pressures of the liquids. Calculation, however, showed that with the wall thickness used, no correction was necessary below 80° in the case of the different mixtures."

All the usual precautions were **taken** to insure reasonable purity of materials used. The sulfur dioxide was obtained from Baker and Company in small iron tanks. It was bubbled through six wash bottles in series, the first one being filled with an 85% sulfuric acid solution to remove any sulfur trioxide which might be present and the remainder with concentrated acid. The gas finally passed over several feet of phosphorus pentoxide. To test its purity, the freezing point was determined very carefully in the following manner. About **20** g. of liquid sulfur dioxide was condensed in a freezing-point tube which was so constructed as to permit stirring without admission of any moisture from the air. The temperature was measured by a standardized re-

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[7] Horace Lamb, "Statics," Cambridge University Press, 1916.

sistance thermometer with a Mueller bridge as supplied by Leeds and Northrup. After a sufficient quantity of the sulfur dioxide had been condensed, the temperature of the cooling bath was slowly lowered until crystals formed in the freezing-point tube. It was then kept constant to within one-half of a degree until all the substance was frozen. The freezing point was found to be **−75.45°;** this did not vary more than **0.05°** while freezing was taking place. It was next allowed to melt very slowly, yielding the same figure as above for the melting point. To further test this point, sulfur dioxide was next prepared from pure sodium acid sulfite by treating it with concentrated sulfuric acid. Its melting point was **−75.43 ± 0.01°.** The purity of this latter material being known, the freezing point was taken as **−75.43 ± 0.05".** This is considerably lower than the value given by Walden and Centnerswer, *viz.*, **−72.7".** The Landolt and Bomstein tables, however, ascribe a value of −75.2°, to van der Goot. The freezing points being for all practical purposes identical, the gas from the tank was, therefore, used throughout. The benzene was the usual thiophene-free material supplied by Baker and Company and was further purified by several recrystallizations and then dried over sodium.

Proportions of Mixtures.—The wide range in boiling points of the two liquids necessitated special precautions, both in the manner of making the mixtures and in placing them in the density and surface tension tubes. Dry liquid sulfur dioxide was collected in a special glass reservoir from which it could be easily removed. To insure constancy of composition in the case of each series of measurements, it was necessary to prepare a considerable quantity of solution. This was done in the following manner. A thick-walled pyrex tube was sealed at one end and the other end sealed to a well-ground glass stopcock in such a way as to form a right angle. This container, after having been thoroughly cleaned and evacuated, was partially filled with a definite amount of benzene. Sulfur dioxide was next introduced until a solution was obtained which was approximately of the composition desired. The exact composition was then determined by weighing the tube. Distillation as a means of transferring the solution from the container to the different tube was out of the question, hence it was necessary to make sealed connections in every case and allow the solution, by inverting the container, to flow into the measuring apparatus. At the completion of each series of measurements, the composition of each solution was checked by allowing the sulfur dioxide to dissolve in alkaline solution of known strength and then titrating.

Measurement of Surface Tension.—All the temperatures were measured by a resistance thermometer which had been standardized by the U. S. Bureau of Standards and tested from time to time by determining the freezing point of water. The cathetometer could be read directly to 0.05 mm. and its accuracy was insured by focusing on a standard meter scale, standing upright beside the constant temperature bath.

Measuring the height of the liquids beolw 0° was found to be a rather difficult task. The difficulties increased with fall of temperature. Following the instructions of Richards, readings were always taken with a falling meniscus. This, however, as pointed out by Harkins and others, is apt to give too high a reading, unless sufficient time is allowed for the adhering liquid to drain back. Owing to the viscosity of sulfur dioxide at low temperatures, this required a considerable length of time. Indeed, the time required before the difference in height of the menisci became constant, when dealing with pure oxide at −50°, was between five and six hours. Irregularities in the heights and rates of fall such as are described by Bigelow and Washburn[8] when studying the variations in the surface tension of solutions were noticed. As these variations were more pronounced at low temperatures, they were at the time ascribed to the viscosities of the solutions.

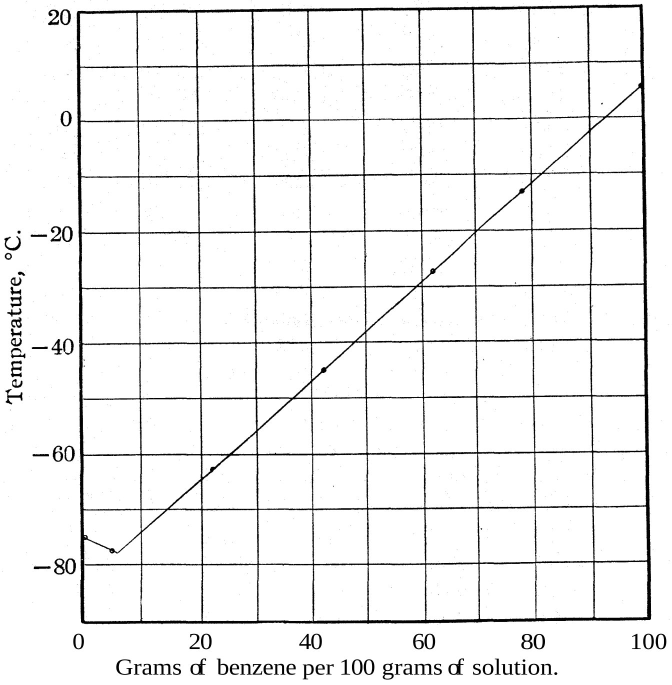

Fig. 4.—The freezing-point curve of benzene–sulfur dioxide solutions.

The densities and surface tensions of pure sulfur dioxide and of the solutions are given in the following tables. The vapor densities of the pure liquid from −50 to 0° were calculated by means of the perfect gas law and above zero by the law of Cailletet and Mathias. In calculating the vapor densities of the solutions the validity of Raoult's Law and the perfect gas law were assumed. The values of Ke were obtained by first plotting on a large scale the molecular surface energies against temperature and then calculating the constant by means of the values taken from the smoothed curve. The molecular weights in the case of the solutions were taken as

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[8] Bigelow and Washburn, *J. Phys. Chem.*, **32**, **1** (1928).

the mean of the two. Tables showing the relationships between concentrations and freezing points, and concentrations and total surface energies, are also given.

TABLE I

DENSITIES AND SURFACE TENSIONS OF PURE SULFUR DIOXIDE

Temp., °C.	Density corr. for vacuum	Density of vapor	Diff. in height corr. cm.	Surface tension, dynes	Mol. surface energy, ergs	Eötvös constant, Ke
−50	1.5590	0.0004	1.470	34.48	410	1 6
−40	1.5349	.0007	1.415	32.69	393	
−30	1.5106	.0012	1.365	30.91	376	
−20	1.4863	.0020	1.315	29.33	361	
−10	1.4619	.0027	1.265	27.73	344	1 8
0	1 4368	.0029	1.200	25 83	324	
10	1.4113	,0037	1.135	24.05	305	
20	1.3848	.0052	1.070	22.19	285	2.1
30	1.3574	.0073	1.000	20.30	265	
40	1.3296	.0101	1.920	18.23	241	
50	1.3007	.0140	0.850	16.43	219	2.1
60	1.2695	.0202	.785	14.73	199	
70	1.2360	.0287	.715	12.86	179	
80	1.1979	.0318	.635	11.03	155	
90	1.1568	.0479	.560	9.33	133	
100	1.1119	.0678	.485	7.60	110	

TABLE II

SOLUTION No. 1. DENSITIES AND SURFACE TENSIONS OF SOLUTION CONTAINING 77.7% BY WEIGHT OF BENZENE

Temp., °C.	Density corr. for vac.	Density corr. for vapor	Diff. in height corr.. cm.	Surface tension, dynes	Mol. surface energy, ergs	Eotvds constant, Kc
−10	0.9926	0.9917	2.136	31.83	571	2.2
0	.9799	.9787	2.051	30.16	545	
10	.9662	.9635	1.976	28.61	523	
20	.9543	.9510	1.901	27.16	502	
30	.941	.937	1.826	25.72	480	2.2
40	.929	.923	1.751	24.30	458	
50	.916	.909	1.676	22 90	437	
60	.904	.894	1.601	21.57	415	2.2
70	.892	.879	1,526	20.08	394	
80	.879	.863	1.446	18.75	371	

TABLE III

SOLUTION NO. 2. DENSITIES AND SURFACE TENSIONS OF SOLUTIONS CONTAINING 62.69% BY WEIGHT OF BENZENE

Temp., °C.	Density corr. for vac.	Density corr. for vapor	Diff. in height, corr., cm.	Surface tension, dynes	Mol. surface energy, ergs	Edtvds constant, Ke
−30	1.0761	1.0758	2.090	33.79	560	2.2
−20	1.0625	1.0619	2.010	32.08	537	
−10	1.0491	1.0481	1.930	30.40	515	
0	1.0358	1.0343	1.850	28.76	489	

TABLE IXI (*Concluded*)

Temp., °C.	Density corr. for vac.	Density corr. for vapor	Diff. in height, corr., cm.	Surface tension, dynes	Mol. surface energy, ergs	Eötvös constant, Ke
10	1.0221	1.0195	1.770	26.95		2.2
20	1.008	1.004	1.695	25.59		
30	0.994	0.989	1.620	24.09		
40	.980	.973	1.545	22.53	397	
50	.967	.957	1.470	21.21	377	2.1
60	.954	.940	1.390	19.73	355	
70	.938	.922	1.320	18.29	332	
80	.923	.902	1 250	16.95	311	

TABLE IV

SOLUTION NO. 3. DENSITIES AND SURFACE TENSIONS OF SOLUTIONS CONTAINING 46.01% BY WEIGHT OF BENZENE

Temp., °C.	Density corr. for vac.	Density corr. for vapor	Diff. in height, corr., cm.	Surface tension, dynes	Mol. surface energy. ergs	Eötvös constant, Ke
−30	1.1191	1.1186	1.620	33.50		2.5
−20	1.1044	1.1035	1.545	31.45		
−10	1.0897	1.0882	1.470	29.52	476	
0	1.0741	1.0718	1.405	27.84	453	
10	1.0585	1.0549	1.335	26.04	428	2.3
20	1.047	1.042	1.270	24.42	405	
30	1.037	1.030	1.205	22.90	382	
40	1.026	1.017	1.140	21.39	360	
50	1.013	1.000	1.070	19.79	360 337	
60	1.001	0.992	1.000	18.26	315	2.2
70	0.985	.962	0.9355	16.84	294	
80	.977	.947	.8755	15.33	271	

TABLE V

SOLUTION NO. 4. DENSITIES AND SURFACE TENSIONS OF SOLUTIONS CONTAINING 22.07% BY WEIGHT OF BENZENE

Temp., °C.	Density corr. for vac.	Density corr. for vapor	Diff. in height, corr., cm.	Surface tension, dynes	Mol. surface energy, ergs	Eötvös constant, Ke
−60	1.2969	..	1.615	38.72	537	2.1
−50	1.2812	..	1.555	36.79	515	
−40	1.2630	..	1.495	34.91	493	
−30	1.2468	..	1.440	33.19	473	2.2
−20	1.2313	1.2300	1.380	31.38	451	
−10	1.2149	1.2127	1.320	29.53	428	
0	1.1962	1.1929	1.250	27.57	404 381	
10	1.1784	1.1734	1.185	25.78		2 3
20	1.160	1.153	1.120	23.88	358	
30	1.141	1.131	1.055	22.06	335	
40	1.122	1.109	0.990	20.31	312	
50	1.103	1.085	.925	18.56	290	
60	1.083	1.060	.855	16.76	266 .	
70	1.062	1.030	.785	14.95	241	
80	1.040	1.000	.715	13.23	218	

TABLE VI

FREEZING POINTS OF BENZENE–SULFUR DIOXIDE SOLUTIONS

Benzene, % by wt.	0	5.5	22.0	46 0	62.6	77.7	100
F. p., °C.	−75 43	−77.4	−61.1	−41.0	−26.5	−13.6	5.4

TABLE VII

TOTAL SURFACE ENERGIES OF PURE LIQUIDS AND SOLUTIONS, ERGS PER SQ. CM. AT 0°

Benzene, % by wt.	0 (pure SO_2)	22.0	46	62.6	77.7	100
Surf, energ., ergs	74.6	76.4	77.5	78.2	69.9	67.2

Discussion of Results

The densities found for the pure sulfur dioxide are slightly higher than the mean of those given in the critical tables. The surface tensions on the other hand are somewhat lower than those found by V. M. Stowe.[9] From the results obtained sulfur dioxide appears to be associated at temperatures below 20°, which is to be expected from the polar nature of the molecule. With reference to the solutions it is seen that *Ke* is greater in all cases than is either that of benzene (2.13) or of sulfur dioxide, which on the basis of the Walden and Swinne relationship between the value of *Kc* and the size of the molecule would indicate the existence of a larger molecule in the case of the solutions than is found in either of the two pure liquids. The simplest solvate molecule conceivable, although the freezing-point curve gives no indication of such, would be one molecule of benzene combined with one of sulfur dioxide which, by applying the equation discovered by the above-mentioned authors, $Ke = 1.90 + 0.011\,(\Sigma\sqrt{n\mathrm{A}})$ where $\Sigma\sqrt{n\mathrm{A}}$ represents the sum of the square roots of the atomic weights of the elements comprising the molecule, calls for a value of *Ke* equal to *2.34*. Solutions Nos. 2 and 3 apparently fulfil this condition at temperatures below 0°, the complex-molecule decomposing as the temperature rises. Solution No. 1 gives a constant value of *Ke* over the temperature measured. Its low value may be accounted for by assuming it to be the average of that of the excess benzene and that of the solvate. Solution No. 4 unfortunately shows an increasing value of *Ke*. It is difficult to find a satisfactory explanation to account for this increasing value on the basis of the above theory. Of course, at higher temperatures than 80° a decrease in the value of *Ke* might take place As this solution was composed of 77.93% of sulfur dioxide the value of 2.23 obtained at the temperatures below 0° might be due to the fact that some of the molecules of the sulfur dioxide were associated. If now the associated molecules were to break up faster than the solvate molecules as the temperature rose, a larger value of *Ke* would result. Irregular variations in the value of *Ke* are recorded by Ramsay and Aston.[1] Variations in the value of *Ke* with temperature are not limited to solutions but occur in nearly all pure liquids which are composed of com-

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[9] Stowe, THIS JOURNAL, 51,410 (1929).

plicated and rather unstable molecules. Thus Jaeger[4] found, to give only a few examples, that ethyl acetate has a value of Ke between −74 and 0° of 2.50, which gradually falls to a value of 1.30 above 15°. A few cases show increasing values of *Ke* with rising temperature, *e. g.*, diethyloxalic acid has a value of 1.8 below 0°, which rises to 3.6 at temperatures above 146°. In still other cases the value of Ke passes through a minimum. While inaccuracies in measurement might be the cause of small variations in the value of Ke, as suggested by Livingston and Morgan,[10] they can scarcely be held to account for the gradual drift in the up or down value of *Ke*. In any case it appears that liquids composed of complicated molecules behave as do binary mixtures.

A satisfactory explanation of the foregoing will likely be found in a combination of surface absorption theories and that of orientation as put forward by Hunten and Maass.[11]

Summary

1. The freezing points, densities and surface tensions of pure sulfur dioxide and of sulfur dioxide and benzene solutions have been measured.
2. It has been shown that sulfur dioxide is associated at low temperatures.
3. The freezing-point curve shows no compound formation.
4. The values of the Eotvos constant for binary mixtures have been shown to be dependent upon concentration and temperature.

VANCOUVER, B. C., CANADA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 229]

A COMPARISON METHOD FOR DETERMINING IONIZATION CONSTANTS WITH A QUINHYDRONE REFERENCE ELECTRODE

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Introduction

Within recent years, the potentiometric method[1,2] of determining ionization constants of weak acids has begun to displace the conductivity method. One disadvantage of the latter is that it is necessary to make conductance measurements not only of solutions of the acid but also of those of a salt of the acid in order to compute Λ_0; another disadvantage arises from the fact that in order to obtain moderately accurate results very pure water must be used for the preparation of the dilute solutions.

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[10] Livingston and Morgan, THIS JOURNAL, **33**, **643** (1911).

[11] Hunten and Maass, *ibid.*, **51**, 153 (1929).

[1] Britton, *J. Chem. Soc.*, **127**, 1896 (1925); Auerbach and Smolczyk, *Z. physik. Chem.*, **110**, 65 (1924).

[2] Kuhn and Wassermann, *Helv. Chim. Acta*, **11**, 31 (1928).

The usual potentiometric method in which the acid is titrated with a standard base to give a titration curve is not entirely satisfactory since (1) the accuracy of the constant is seriously affected by the difficulty of determining the inflection point in the voltage–ml. plot when the acid is weak, and (2) the liquid junction potentials vary while the titration is being carried on, due to the continued addition of water and of the positive ion. The method described in this paper has an advantage over the titration method in that the liquid junction potentials are for the most part eliminated.

Method

The method consists in determining the potential of the reference electrode represented at the left end of the cell below, first against a saturated solution of quinhydrone containing hydrochloric acid at various concentrations, and then against similar solutions containing the acid under investigation at a series of concentrations. The whole cell may be represented thus

Pt, KCl(0.09 N) + HCl(0.01 N) + Quinhydrone
KCl(0.09 N), HA(*c* N) + Quinhydrone, Pt

HA represents hydrochloric acid in one series of measurements and the acid under investigation in the other series.

From the data obtained when hydrochloric acid is used a curve is drawn by plotting the measured voltages against the logarithms of the mean ion activities, $C\alpha$ of the hydrochloric acid. When any other acid is used as HA in the above cell, it is possible to obtain the logarithm of the mean ion activity of this acid at any concentration from the corresponding voltage.

It is difficult to evaluate the liquid junction potentials when the junction is being continuously renewed, but it seems certain that the difference between the liquid junction potential when hydrochloric acid is used and when an organic acid of the same mean ion activity replaces it will introduce an error in the constants well within the limit of experimental error of the measurements.

Calculation of the Constant.—The ionization constant is calculated from the experimental data by means of the expression

$$K_A = \frac{a_{\pm}}{\left(C - \frac{a_{\pm}}{\alpha}\right)}$$

where $a_{\pm}$ is the mean activity of the ions, C is the molal concentration of the acid, and α is the mean activity coefficient.

This assumes (1) that the activity of the undissociated acid is equal to its concentration, (2) that the mean ion activity in the organic acid solution is the same as the mean ion activity in that hydrochloric acid solution which gives the same potential against the reference cell and (3) that the quinhydrone will affect the mean ion activity to the same extent in solutions of the same mean ion activity.

'She work of Randall and others[3] shows that at the concentrations of acid (0.02–0.0003 M) used in these measurements the first assumption is **fully** justified. Since the determination of the individual ion activities is a difficult operation, it is desirable to make the second assumption, which seems justifiable at the low concentrations of ions prevailing.

The solubility of the quinhydrone is small,[4] 0.018 mole per liter at 25°, and presumably about the same in the various solutions so that the last assumption is a reasonable one.

Apparatus and Materials

The cell used was similar to the type proposed by Kohn[5] and is shown in the figure, The inner cell containing the reference solution consisted of a glass tube 1.5 cm. in diameter and 15 cm. in length fitted with a ground-on glass cap and a removable electrode carrying a piece of bright platinum foil. The outer cell consisted of a 400-cc. beaker fitted with a rubber top through which passed the mechanical stirrer, the nitrogen bubbling tube, the inner cell and a glass tube carrying a piece of bright platinum foil which served as the second electrode.

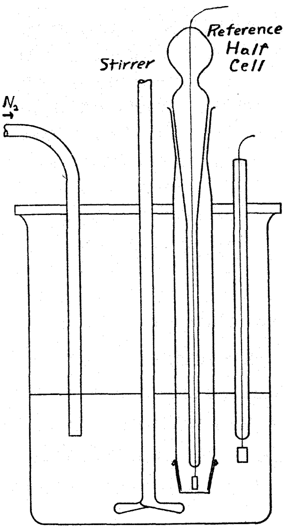

Fig. 1.

The e.m.f. measurements were made with a Leeds and Northrup Type K potentiometer. The cell was immersed in an oil thermostat maintained at 25 ± 0.02".

Eastman's quinhydrone was recrystallized twice from water at 70° and was dried over sulfuric acid in a vacuum desiccator.

Constant boiling hydrochloric acid was prepared by the distillation in an all-pyrex apparatus of concentrated C. P. hydrochloric acid previously diluted to a specific gravity of 1.11. At the observed pressure of 744.6 mm[6] one mole of hydrogen chloride is contained in 179.864g. of solution. A tenth-normal solution was prepared by diluting a weighed amount of this standard acid with a weighed amount of water. Lower concentrations were made by volume dilutions from this solution.

The potassium chloride was recrystallized four times from hot water and fused to dryness.

Benzoic acid of standard quality was purified by three crystallizations from hot water and a subsequent sublimation.

The *p*-cyanobenzoic acid was the same as that used in the research of Valby and Lucas.[7] A stock solution was prepared by dissolving a weighed quantity of the solid organic acid in water to a definite volume. This stock solution was diluted by volume to obtain the lower concentrations.

The water used in the preparation of all solutions was obtained by distillation of distilled water from sodium carbonate and potassium permanganate in an all-pyrex

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[3] Randall and Failey, *Chem. Reviews,* 4,291 (1927).

[4] Biilman, Ann. *chim.,* 15,113 (1921).

[5] Kohn, *Z. angew. Chem., 39,* 1073 (1926).

[6] Foulk and Hollingsworth, THIS JOURNAL, 45, 1225 (1923).

[7] Valby and Lucas, *ibid.,* 51,2718 (1929).

apparatus in an atmosphere of nitrogen. Care was taken to prevent absorption of carbon dioxide and oxygen from the atmosphere.

Experimental Method

The glass cap of the reference half-cell was filled with 0.09 *N* potassium chloride solution and fastened to the cell with a rubber band. This provided a bridge of 0.09 *N* potassium chloride through the ground-glass joint. The excess liquid was removed by three washings with the reference solution and the half-cell filled to a depth of 3–4 cm. with the reference solution. The liquid levels were kept about the same in the outer and inner half-cells to minimize the drift in potential due to diffusion through the ground-glass joint during the measurements. To the 400-cc. beaker which served as the outer half-cell was added about 200 cc. of the hydrochloric or organic acid solution. The outer parts of the reference half-cell were washed with a small amount of the same solution, the two half-cells were assembled in the oil thermostat and connected to the potentiometer. Stirring was carried on at a slow rate by the motor-driven stirrer while purified nitrogen was passed through the outer half-cell at the rate of about 20 bubbles a minute. Voltage readings were made at five-minute intervals until equilibrium to within 0.1 millivolt was attained, which generally took from ten to fifteen minutes. This equilibrium value was usually about one millivolt lower than the initial reading. The bright platinum foil electrodes were found to give reproducible results throughout the entire series of measurements.

The reference half-cell was filled anew before each determination, since otherwise the observed voltage on a succeeding run would be materially lower.

All solutions used were saturated with quinhydrone at 45° by vigorous shaking for fifteen minutes in the presence of a small excess of the solute. The solutions were then brought to 25° by immersion in the thermostat and were shaken at intervals to aid crystallization of the excess quinhydrone.

Reference Curve.—Using the apparatus and methods described, measurements were made of the voltages produced by solutions of known concentrations of hydrochloric acid saturated with quinhydrone against the reference solution 0.09 N in potassium chloride and 0.01 *N* in hydrochloric acid, saturated with quinhydrone. The results are given in Table I.

TABLE I

DATA FOR THE CONSTRUCTION OF THE REFERENCE CURVE

Concn. of HCI, moles per liter	*Log a*	Log αC	Observed e.m.f., volts	Concn. of HCI, moles per liter	*Log a*	Log αC	Observed e.m.f., volts
0.01023	−0.0432	$\bar{3}.9669$	+0.0020	0.000511	−0.0110	$\bar{4}.6974$	−0.0725
.01023	− .0432	$\bar{3}.9669$	+ .0026	.000204	− .0075	$\bar{4}.3021$	− .0963
.01023	− .0432	$\bar{3}.9669$	+ .0021	.000204	− .0075	$\bar{4}.3021$	− .0950
.01023	− .0432	$\bar{3}.9669$	+ .0025	.0001023	− .0050	$\bar{4}.0051$	− .1126
.00511	− .0325	$\bar{3}.6759$	− .0142	.0001023	− .0050	7.0051	− .1157
.001023	− .0151	$\bar{4}.9950$	− .0544	,0001023	− .0050	$\bar{4}.0051$	− .1161
.001023	− .0151	$\bar{4}.9950$	− .0543	.0001023	− .0050	$\bar{4}.0051$	− .1174
.001023	− .0151	$\bar{4}.9950$	− .0533	.00001023	− .0009	$\bar{5}.0090$	− .1745
.001023	− .0151	$\bar{4}.9950$	− .0568				

The activity coefficients at the higher concentrations are those of Randall and Young.[8] At concentrations below 0.001 *N* the activity coefficients

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[8] Randall and Young, This Journal, ,50,989 (1928).

were calculated by means of the Debye–Hückel equation.[9] The observed voltages were plotted against the corresponding values of log αC and a straight line was drawn through the points. The curve may be reproduced from the values given in Table II.

TABLE II

INTERPOLATED VALUES OF VOLTAGE AND LOG αC FROM REFERENCE CURVE

Log αC	$\bar{2}$ 000	$\bar{3}$.000	$\bar{4}$ 000	$\bar{5}$ 000
Voltage	+0 0045	−0.0646	−0 1138	−0 1728

The small amount of carbon dioxide which may have contaminated the solution in spite of the precautions taken would not modify the curve appreciably in the region employed.

Application of the Method

In Table III are tabulated the data obtained with benzoic and *p*-cyanobenzoic acids, using the apparatus and experimental technique previously described.

TABLE III

RESULTS WITH BENZOIC AND *p*-CYANOBENZOIC ACIDS

Benzoic Acid				*p*-Cyanobenzoic Acid			
Acid concn., moles per liter	Observed e.m.f.	Log $\alpha_{\pm}$	K_A X 105	Acid concn , moles per liter	Observed e.m f.	Log $\alpha_{\pm}$	$K_A \times 10^5$
0.02129	−0.0511	$\bar{3}$.057	6.47	0.007294	−0.0465	$\bar{3}$.135	3.17
.01065	− .0598	$\bar{4}$.910	6.73	.007294	− .0465	$\bar{3}$.135	3.17
.01065	− .0595	$\bar{4}$.915	6 90	.003647	− .0570	$\bar{4}$.960	3.08
.004258	− .0719	$\bar{4}$ 706	6.90	.003647	− .0570	$\bar{4}$.960	3.08
.004258	− .0720	$\bar{4}$.705	6 87	.001459	− .0707	$\bar{4}$.727	3.01
.002129	− .0819	$\bar{4}$ 538	6 72	.001459	− .0704	$\bar{4}$.732	3.12
.02032	− 0517	$\bar{3}$ 047	6 49	.0007294	− .0823	$\bar{4}$.531	3.02
.02032	− ,0511	$\bar{3}$ 057	6 64	.0007294	− .0823	$\bar{4}$.531	3.02
.01016	− .0606	$\bar{4}$.888	6 38	.0003647	− .0946	$\bar{4}$.325	2.99
.01016	− .0603	$\bar{4}$ 902	6 82		Av. 3.10 ± 0.10 × 10^{-4}		
.004064	− .0725	$\bar{4}$ 695	6 90				
.001016	− .0926	$\bar{4}$ 351	6 38				
	Av., 6.68 ± 0.25 X 10^{-5}						

The values of the logarithm of the mean ion activity in the organic acid solutions were obtained from the plot of the data of Table I. The values of the constant were calculated from the expression $K = a_{\pm}/(C - (a_{\pm}/\alpha))$. These values were then plotted against the logarithm of the concentration to obtain the constants at round concentrations which were compared in the case of benzoic acid in Table IV with those of some previous investigators obtained from conductance measurements.

It is seen that the values obtained by any one investigator agree very well but the divergence of the results of different investigators is quite con-

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[9] Noyes, THIS JOURNAL, **46,** 1080 (1924).

siderable. These constants were calculated using ion concentrations rather than mean ion activities, but this difference is much less than the variation in results.

TABLE IV

K_A OF BENZOIC ACID BY DIFFERENT INVESTIGATORS[10]

Concn.	Ostwald	Euler	Schaller	Kortright	White and Jones	This paper
0.02	5.98	6.68	6.80	6.19	6.70	6.63
.01	5.98	6.67	6.77	6.30	6.77	6.84
.004	6.04	6.70	6.84	6.31	6.87	6.86
.002	6.05	6.69	6.77	6.34	6.83	6.76
.001	5.89	6.69	6.61	6.41	6.51	6.50

The maximum deviation from the mean in the values for the ionization constant of *p*-cyanobenzoic acid is 3%. The mean value agrees with the value of **3.09** X 10^{-4} which Valby and Lucas[7] obtained by the conductance method.

Summary

Ionization constants of organic acids may be determined by means of a quinhydrone cell in which the reference half-cell is standard hydrochloric acid solution saturated with quinhydrone and containing potassium chloride.

The method is tested in the case of benzoic acid by a comparison of the values herein obtained with those reported by previous investigators and found to be in satisfactory agreement.

The ionization constant of *p*-cyanobenzoic acid is found to be $3.10 \pm 0.10 \times 10^{-4}$. This result likewise agrees well with the value recently obtained by the conductance method.

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[10] Ostwald, *Z. physik. Chem.*, *3*, 241 (1899); Euler, *ibid.*, 21, 257 (1896); Schaller, *ibid.*, 25, 497 (1898); Kortright, *ibid.*, 21, 311 (1896); White and Jones, Am. *Chem. J.*, *44*, 159 (1910).

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

THE BEHAVIOR OF GLASS ELECTRODES OF DIFFERENT COMPOSITIONS

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In a recent article[1] the authors have described a new form of glass electrode which can be made of small size, but with sufficiently low resistance for accurate work. The design of the electrode is shown in Fig. 1. The supporting tube B (which is usually about 4 mm. in diameter) holds the thin glass diaphragm D over its lower end. The tube is partially filled with hydrochloric acid (0.1 N in our experiments) into which is inserted a silver–silver chloride electrode C. The upper part of tube B is coated, inside and outside, with paraffin.

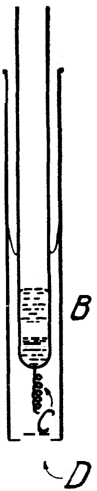

Fig. 1.

In the experiments to be described below the diaphragm D and supporting tube B were made as follows. A piece, weighing about 50 mg., of specially prepared glass for the diaphragm was first melted into the end of a pyrex tube of about 4 mm. diameter. The glass was then heated to a low red heat and blown into the form of a bubble with walls thin enough to show interference colors. The end of the tube B, which was of ordinary soft glass, was heated somewhat under red heat, and was then brought into contact with the bubble wall. If this operation is properly carried out the diaphragm will fuse onto the lower edge of the tube B. Such diaphragms are surprisingly strong. A group of tubes having these diaphragms over their lower ends held columns of nine centimeters of mercury for three weeks or more. No apparent difference in this time was observed whether the diaphragm was placed in tenth-normal acid or alkali or in water. The diaphragms are, however, easily broken by sudden jars.

The present investigation was undertaken with the purpose of finding the most suitable glass for the diaphragm.[2] The design of glass electrode just described is better than the original Haber form for comparing different samples of glass, since diaphragms of very nearly uniform and definite thickness can be selected and fused onto tubes of sufficiently uniform bore. Since commercial glasses are available with narrow ranges of composition

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[1] MacInnes and Dole, *Ind. and Eng. Chem. (Analytical Edition),* 1, 57 (1929). This article contains references to the earlier work on the glass electrode. An apparatus involving the application of these electrodes to the determinaton of the hydrogen-ion concentration of very small amounts of liquids is described in J. *Gen. Physiol.*, 12, 805 (1929).

[2] Tests of commercial glasses, using the Haber form of glass electrode, have been made by Hughes, J. *Chem. Soc.*, 491 (1928), and Elder, THIS JOURNAL, 51, 3266 (1929).

only and contain a large number of components, some of which are definitely undesirable, it was decided to make our own samples of glass. These new glasses have, however, been compared with some commercial specimens. With the aid of Dr. Geo. W. Morey, to whom we are much indebted for assistance and suggestions, a platinum–rhodium wound furnace such as he has used in his researches on glass was constructed in the shop of the Geophysical Laboratory. The furnace is capable of reaching temperatures up to 1600°. We have also received useful suggestions from the Staff of the Bureau of Standards.

In making the glasses dry silica, calcium or magnesium carbonate and the carbonate of the alkali used were weighed out in the desired proportions and thoroughly mixed by grinding. The mixture was then melted in the furnace. It was found convenient to add the mixture a few grams at a time; otherwise the evolution of carbon dioxide causes the melt to flow over the edge of the crucible. After melting the sample it was held for an hour or so at 1200 to 1400° until all gas bubbles escaped from the melt, and to insure uniformity. The crucible and contents were then cooled, at first slowly and finally by quenching in a stream of cold water. This yielded material cracked into small pieces, some of which were suitable for making the thin diaphragms as already described.

For a first survey of the possible suitability of a glass for use as an electrode, three properties were measured, after the glass had been made into electrodes of the form shown in Fig. 1 with diaphragms of approximately 4 mm. diameter and about 0.001 mm. thickness. The properties chosen were (a) the potential existing in the diaphragm, (b) the resistance of the electrode and (c) the deviation from the theoretical potential when the electrode was placed in a buffer solution at P_H 8, and in an approximately 0.1 N sodium hydroxide solution of P_H 12.75.

(a) The potential in the glass was measured because, in the first place, it is a correction to the measured potential which must be made when the electrode is used for determining hydrogen-ion activities. Further, we have found by experience that if this "asymmetry potential" is large it is also likely to be varying and to require frequent determination. In addition, a glass with a large asymmetry potential is almost certainly otherwise unsuitable. The asymmetry potential was obtained by measuring the e.m.f. between the glass electrode and a silver–silver chloride electrode when both were placed in 0.1 N hydrochloric acid.

(b) The electrical resistance of the glass must not be too large, because a high resistance lowers the sensitivity of the measurements, and makes elaborate screening and insulation of the measuring instruments and of the cell necessary. Measurements of the resistance of the electrodes were carried out by shunting the electrometer with a 0.5 megohm resistance, after which it was connected in a circuit containing the glass electrode placed in hydrochloric acid, a silver–silver chloride electrode in the same solution and a known potential (1.2 volts). From the deflections obtained the resistances of the electrodes could be computed. With some of the harder glasses this method failed to yield quantitative measurements since the electrometer deflections were very small or zero, but in these cases the glasses were of no use for our purpose.

(c) To measure the effectiveness of a glass when used as an electrode for determining hydrogen-ion activity, the glass electrode was placed first in a buffer solution of PH 8 with which a saturated calomel electrode was connected, the arrangement being

$$\text{Hg} \mid \text{HgCl, KCl (satd.)} \parallel \text{soln. } \mathbf{A} \mid \text{glass} \mid 0.1\ N\ \text{HCl, AgCl} \mid \text{Ag}$$

If the glass surface is reversible to the hydrogen-ion activity, this combination can readily be seen to be equal in potential to the sum of the two cells

$$\text{Hg} \mid \text{HgCl, KCl (satd.)} \parallel \text{soln. } \mathbf{A} \mid H_2 \text{ and } H_2 \mid \text{HCl } (0.1\ N)\text{, AgCl} \mid \text{Ag}$$

The potential of the first of these cells[3] is at 25°

$$E = 0.2458 - 0.05915 \log a_H$$

(in which a_H is the hydrogen-ion activity of solution A) and of the second −0.3524.[4] The relation between the e.m.f. of Cell 1 and the hydrogen-ion activity is, therefore, at 25°

$$E = -0.1066 - 0.05915 \log a_H = -0.1066 + 0.05915\ P_H$$

If, therefore, the glass surfaces are reversible to the hydrogen-ion activity Combination 1 should have a potential of 0.3663 when Solution A is at *PH* 8 and of 0.6475 in the approximately 0.1 N sodium hydroxide which had a measured *PH* of 12.75. Any glass at all suitable for our purpose showed no deviations in the first test but in the strong alkali large variations from the theoretical potential were always observed.

A summary of the results of the three tests just outlined made on a series of glasses is given in Table I. If the composition of a glass is given in the table it was made in this Laboratory. Most of the figures given in the table are the average of measurements on several electrodes. Though an effort was made to make the diaphragms of the electrodes of the different glasses as nearly alike as possible in diameter and thickness, it was impossible to avoid some variation. However, it will be seen that the effects of changing composition are much larger than can be accounted for by any possible uncertainty in these dimensions. An idea of the reproducibility can be gained from the measurements of resistances of five electrodes made of glass No. 6, the measurements being 11.6, 10.6, 11.1, 15.0 and 10.7 megohms. This degree of reproducibility is possible be-

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[3] W. M. Clark, "The Determination of Hydrogen Ions," The Williams and Wilkins Co., Baltimore, 3d ed., 1928, p. 314.

[4] From the results of Scatchard, THIS JOURNAL, 47, 641 (1925), involving a slight interpolation.

cause a fair estimate of the thickness of a given portion of a glass membrane can be obtained from the interference colors present. It will be seen that the hard glasses, which are the first mentioned in the table, have large potentials present in the diaphragm, large resistances and large deviations from the theoretical potential in alkaline solutions. An improvement in all these respects is to be noted in the "soft commercial" glass (No. 4 in Table I), which showed a rather high but rapidly decreasing membrane potential. The resistance of the electrodes is lower (about **100** megohms), which makes more accurate measurement possible. This resistance, however, increased with time. The error observed in the alkali solutions is also smaller than with the harder glasses.

A great gain in each respect is found in the soft glasses (5 and 6) prepared in this Laboratory. No. 5 has the same composition as that tested by Elder and Wright[5] and is intermediate in properties between the soft commercial glass and No. 6, which has very nearly the composition corresponding to the lowest temperature found on Morey's[6] triangular melting-point diagram for the system $CaO-SiO_2-Na_2O$. This glass is, so far as our experiments have been able to determine, the best for use in determining hydrogen-ion activity. There is a low, nearly zero, potential in the membrane, the resistance is low, and the error in alkaline solution is the smallest observed. A more detailed study of the e.m.f. relations when this glass is made into electrodes is given below.[7]

Glass No. 7 made by increasing the percentage of alkali and decreasing the lime, is definitely too soft. The errors obtained in alkaline solutions are large and increase rapidly. Glasses Nos. 8 to 11 were made by systematically varying the composition of the three components by small percentages from that of glass No. 6. All these samples were inferior to that glass in the constancy of the readings in alkaline solutions, if not inferior in other qualities.

Since suitable glasses for hydrogen-ion measurements are all very soft their solubility may lead to errors if they are used with unbuffered solutions for any length of time. Direct measurements have shown that glass No. 6 will give off about 7×10^{-10} equivalent of base in twenty-four hours per square millimeter of surface. We therefore recommend that the diaphragm only be made of this glass, and that ordinary soft glass be used for the supporting tube.

It seemed possible that a "finer grained" glass might be prepared which

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[5] Elder and Wright, *Proc. Nat. Acad. Sci., 14,* 936 (1928). This composition is recommended by Hughes, J. *Chem. Soc., 491* (1928), but the glass he actually tested varied somewhat from this.

[6] Morey, *J. Soc.* Glass *Tech., 9,* 232 (1925); "International Critical Tables," McGraw-Hill Book Co., Vol. II, p. 97.

[7] The Corning Glass Co., Corning, N. Y., can usually furnish this glass (their Number *015).*

TABLE I

PROPERTIES OF GLASSES AS ELECTRODES

No.	Glass	Composition of glasses, wt percentage SiO$_2$	CaO	Li$_2$O	Na$_2$O	Potential in glass, millivolts 1st day	2d day	Resistance, megohms 1st day	2d day	Initial error in 0.1 *N* NaOH millivolts
1	Pyrex							Very high		
2	Potassium	72	6		22^a	−52.0		High		Rapid incr.
3	Jena thermometer					−47.0	−42.7	400		Rapid incr.
4	Soft commercial					−27.9	− 6.0	72	96	Increase
5	Soda lime	72	8		20	+ 4.1	+ 6.1	47	42	Slow incr.
6	Best soda lime	72	6		22	− 3.8	0.6	12	8	−32 (const.)
7	Soda lime	72	4		24	− 2.5		5		Increase
8	Soda lime	70	6		24	− 7.5	− 1.6	7.5	5.8	−32 (very slow incr.)
9	Soda lime	74	6		20	−14.8	− 4.3	20.3	20.7	Slow incr.
10	Soda lime	74	4		22	− 3.3	0	5 4	3.4	Slow incr.
11	Soda lime	70	8		22	− 1.6	− 0.9	19 9	22 0	Slow incr.
12	Lithium	72	6	22		0	+ 1.1	1.5	0.2	Rapid incr.
13	Sodium lithium	72	6	2	20			600		Rapid incr.
14	Sodium lithium	72	6	4	18			High	700	Rapid incr.
15	Potassium lithium	72	6	11	11^a			3000	3000	Rapid incr.
16	Magnesium	64.5	10^b		25.5	−12.0	− 7.5	45	75	Rapid incr.

^{a} K$_2$O. ^{b} MgO.

would show desirable properties in alkaline solution if lithium were substituted for sodium, since lithium has a much lower atomic volume. A glass was therefore made in which the sodium oxide of sample No. 6 was replaced by lithium oxide. This glass (No. 12 in the table) crystallized readily. However, by sudden chilling a workable, very low melting material was obtained which could be blown into thin bubbles. The supporting tube had, however, to be heated to a lower temperature than usual in order to avoid melting the film. The initial resistance of this glass was very low and dropped rapidly, and the e.m.f. reading at *P*H 8, which was correct on the first day, was considerably in error on the second day. The error in strong alkaline solution was initially about the same as with glass No. 6, but increased very rapidly. The glass is quite hygroscopic and becomes cloudy in a few days. Glasses Nos. 13 and 14 were prepared with the idea of discovering whether any desirable effect could be produced by replacing a part of the sodium in glass No. 6 with lithium. The unexpected result was that the electrodes had too high resistances to be of practical use. The errors in alkaline solution were also large and increasing. Electrodes with very high resistances were also obtained when they were made from a glass (No. 15) in which the sodium oxide of No. 6 was replaced by half each of potassium and lithium oxides. Sample No. 16 was made at the suggestion of Dr. Morey, who found that a melt of the composition given would not crystallize after prolonged heating. The measurements show, however, that it has no properties which recommend it for use as a glass electrode.

It next became of interest to determine the range in which measurements made with electrodes constructed of our best glass (No. 6) agree with the hydrogen electrode. An apparatus shown diagrammatically in Fig. 2 was constructed with which a hydrogen electrode H could be compared with a glass electrode G in the same solution. Connection was also made from the vessel containing this solution to a saturated calomel electrode C so that the P_{H} of the solution and the constancy of the hydrogen electrode could be determined. The solution was saturated by a stream of carefully purified hydrogen entering by tube F. Arrangement was also made so that an alkaline solution could be added from the separatory funnel A to the solution in which the electrodes were dipped so that the P_{H} could be progressively increased. By means of the tube D the current of hydrogen also passed through the alkaline solution in the funnel A so that, since no oxygen was introduced, the hydrogen electrodes rapidly came to a new equilibrium when the P_{H} was changed. The results of such a comparison of the glass and hydrogen electrodes are given in Table II. Since the differences at low P_{H} values are inappreciable, the comparison was started at P_{H} 7.72, using a borax–boric acid buffer solution of approximately 0.1 *N* sodium-ion concentration.

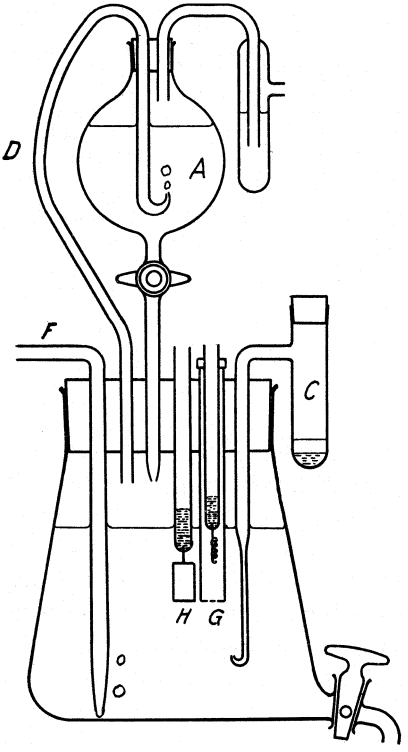

Fig. 2.

TABLE II

COMPARISON OF GLASS AND HYDROGEN ELECTRODES AT DIFFERENT P_{H} VALUES

P_{H}	7.72	8.20	8.73	9.23	9.83	10.47	11.64
Diff. between glass and hydrogen electrodes	0.3540	0.3540	0.3540	0.3540	0.3555	0.3577	0.3688

If the glass surface acts as a hydrogen electrode the potential of the combination

$$H_2 \mid \text{soln. A} \mid \text{glass} \mid 0.1\ N\ HCl, AgCl \mid Ag$$

should be constant and equal to that of the cell

$$H_2 \mid 0.1\ N\ HCl, AgCl \mid Ag$$

whatever the hydrogen-ion activity of solution A may be. The results illustrate the constancy of the difference (within 0.1 millivolt up to P_{H} 9.2) and the deviations to be expected at higher alkalinities. The difference is within 0.0016 volt of the value given by Scatchard[4] for cell (B), the variations possibly being due to a difference in the method of preparing the silver–silver chloride electrodes, and in a lack of control, in these experiments, of the hydrogen pressure. These results are plotted on Curve A in Fig. **3,** together with similar measurements (Curve B) in which the solution between the hydrogen and glass electrodes was kept saturated with sodium chloride (approximately 5.4 N). It will be observed that in this case the deviations from reversibility to the hydrogen activity begin at a lower PH value and are much greater than with the sodium-ion concentration at 0.1 N. The measurements were made with a potentiometer, using a Compton electrometer as a null instrument, in a constant temperature room at 25.0 ± 0.2°. Using glass No. 6 the resistance of the system is so low that ordinary care in screening is sufficient. In our work the leads were covered with a lead sheath, the cell was surrounded by a wire cage, and the necessary switches and tapping key were placed in a tin box. All these screens were, of course, grounded.

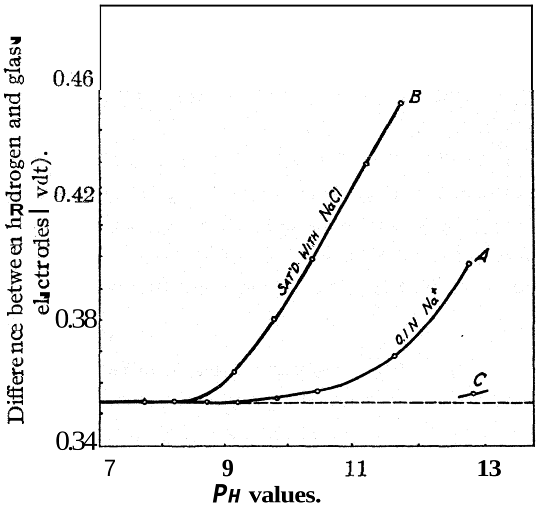

Fig. 3.

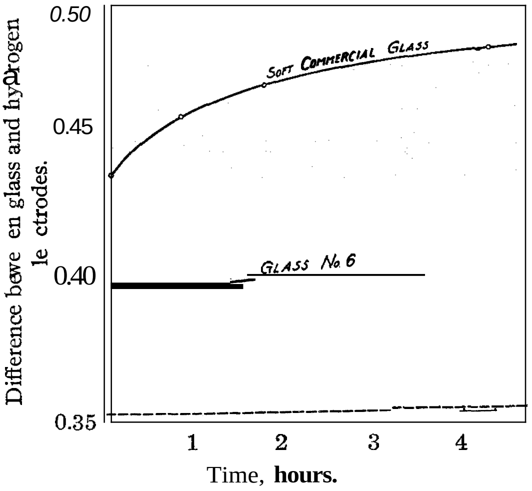

Fig. 4.

Incidentally Curve B also represents with quite sufficient accuracy the measurements of these deviations for glass No. 4 "soft commercial" of Table **I,** with the sodium-ion concentration at 0.1 *N*, showing that our glass No. 6 represents a decided improvement over glasses available in the market in the range of PH values in which the glass electrode is applicable. Furthermore we have observed that glass No. 6 shows steadier potentials in alkaline solution than any other that we have worked with. A comparison of two glasses under somewhat extreme conditions is given in the curves plotted in Fig. 4. The upper curve indicates the variation of the potential with time of the soft commercial glass, and the lower curve the corresponding variation of glass No. 6. It will be seen that the readings of the latter are roughly constant even in these strongly alkaline solutions.

Hughes[2] has shown, however, that these deviations in alkaline solutions depend upon the nature of the positive ions present. We have found, however, very small deviation at about P_H 13 when the base present is tetramethylammonium hydroxide; this is shown in Point C of Fig. 3. We hope to be able to present in the near future a theory explaining these deviations.

Summary

Using a form of glass electrode designed by the authors, the suitability of a series of specially prepared glasses for use as electrodes has been studied, and a few comparisons have been made with samples of glass of commercial origin. The electrodes were tested for "asymmetry potential," resistance and the amount of deviation in alkaline solutions of the measured potential from the theoretically predicted potential. The best of the glasses tested has the composition SiO_2, 72, Na_2O, 22 and CaO, 6%. The potential at the surface of this glass changes quantitatively with the hydrogen-ion activity up to P_H values of 9.5, though this limit is lowered in strong salt solutions.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. X. THE DETERMINATION OF THALLIUM

BY H. H. WILLARD AND PHILENA YOUNG

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Introduction

A number of volumetric procedures for thallium have been proposed. Willm's method based upon the titration of thallous salt in hot hydrochloric acid solution with potassium permanganate has been the one most extensively used.[1] Hawley[1] found that if the permanganate was standardized against pure thallous sulfate in hot solution, using exactly the same

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[1] Willm, *Bull. soc. chim.*, 352 (1863); Noyes, *Z. physik. Chem.*, 9, 603 (1892); Dennis and Doan, THIS JOURNAL, 18, 970 (1896); Marshall, *J. Soc. Chem. Ind.*, 19, 994 (1900); Hawley, THIS JOURNAL, 29, 300 (1907); Müller, *Chem.-Ztg.*, 33, 297 (1909); Berry, *J. Chem. Soc.*, 121, 394 (1922); Bodnár and Terényi, *Z. anal. Chem.*, 69, 29 (1926); Jílek and Lucas, *Chem. Listy*, 23, 124 (1929).

procedure as in a determination of thallium, and if 0.10–0.16 g. of thallium was present, the results were accurate. He showed by a graph that the weight of thallium oxidized by 1 cc. of permanganate was almost constant within this range, but dropped rapidly with less than 0.1 g. of thallium. Berry[1] used the electrometric end-point and found, in agreement with Hawley, that the method was a very empirical one. Jílek and Lucas[1] reported good results if considerable potassium chloride was added to the hydrochloric acid solution of the thallous salt before the titration with permanganate. Nietzki[2] titrated a thallous salt with standard potassium iodide as long as a precipitate formed, obviously an inaccurate method. Feit[3] added potassium iodide and an excess of standard arsenite to a thallic salt, filtered off the thallous iodide and titrated the excess arsenite with standard iodine. His results were low and the method involved a preliminary oxidation of thallous salt. Thomas[4] substituted standard thiosulfate for arsenite. Sponholz[5] titrated a thallous salt with standard bromine water to a visual end-point, an inaccurate method because of the instability of the oxidizing agent and the uncertainty of the end-point. Marshall[1] oxidized a thallous salt, to which bromide was added, with a measured excess of standard sodium bromate in a hydrochloric acid solution, distilled the bromine formed into potassium iodide solution and titrated the iodine with thiosulfate. He stated that the method was rapid and accurate, but it has the disadvantages of requiring a special form of apparatus and two standard solutions. Zintl and Rienäcker[6] simplified this procedure by titrating thallous salt in hydrochloric acid solution with standard potassium bromate, using the electrometric method or methyl orange as internal indicator. Their results were accurate, and the procedure was simple and rapid. These same authors showed that thallic salt could be titrated with standard titanous chloride in acetic acid solution. Browning and Palmer[7] oxidized thallous oxide with ferricyanide in alkaline solution, filtered off the thallic oxide formed, acidified the filtrate with sulfuric acid and titrated the ferrocyanide with standard permanganate. Berry[1] checked this method using recrystallized thallous sulfate, obtained good results by drying the thallic oxide, but found only a fairly good agreement by titrating the ferrocyanide in the filtrate. The color change at the end-point was not sharp. Berry[8] titrated thallous ion in strong

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[2] Nietzki, *Arch. Pharm.*, [2] *4*, 385 (1871).

[3] Feit, *Z. anal. Chem.*, 28, 314 (1889).

[4] Thomas, *Compt. rend.*, 134, 655 (1902).

[5] Sponholz, *Z. anal. Chem.*, *31*, 519 (1892).

[6] Zintl and Rienacker, *Z. anorg. allgem. Chem.*, *153*, 276 (1926).

[7] Browning and Palmer, *Am. J. Sci.*, [4] 27, 379 (1909).

[8] Berry, *Analyst*, 51, 137 (1926). After this paper had been submitted for publication, further work by this author appeared [*ibid.*, 54, 461 (1929)] in which he gave the results of a single titration of thallous chloride by ceric sulfate using iodine chloride

hydrochloric acid solution with potassium iodate, using chloroform as indicator.

Since nearly all of the volumetric methods for thallium except the bromate method of Zintl and Rienäcker[6] have serious disadvantages, the authors felt that a rapid and accurate procedure for thallium would be of value. The following material describes such a method based upon the direct titration of thallous salt with standard ceric sulfate.

Experimental

Very pure thallous sulfate was recrystallized from water, dried at 150° and used to prepare a standard solution. The ceric sulfate solution was prepared by the method described by the authors[9] from high-grade ceric oxide obtained from the Welsbach Company of New Jersey and was 0.5 M in sulfuric acid. It was standardized against sodium oxalate.[10]

Titration in Hydrochloric Acid Solution.—Measured volumes of the standard thallous sulfate solution were taken, diluted with water and acid, heated to the temperature indicated and titrated electrometrically at that temperature with standard ceric sulfate. A silver chloride–platinum

TABLE I

TITRATION OF THALLOUS SALT WITH 0.1 *N* CERIC SULFATE IN HYDROCHLORIC ACID SOLUTION. ELECTROMETRIC END-POINT

Init. vol. soln., cc.	HCl, sp. gr. 1.18, cc.	Temp., °C.	Thallium Taken, g.	Thallium Found, g.	Character of reaction
200	10	58-60	0.1008	?	Too slow, unsatis.
200	20	58–60	.1008	0.1008	Slow, fairly satis.
200	20	65–67	.1008	.1008	Rapid, end-point poor
200	30	58-61	.1008	.1008	More rapid, satis.
200	30	55–57	.1008	.1008	More rapid, satis.
200	30	48–51	.1008	.1008	Slow, fairly satis.
200	40	58-60	.1008	.1009	Rapid, satisfactory
200	40	4446	.1008	.1008	Little slow, satis.
200	50	44-46	.1008	.1008	Rapid, satis.
200	50	34–36	.1008	.1009	Little slow, satis.
200	60	34–36	.1008	.1008	More rapid, satis.
200	60	30–31	.1008	.1005	Little slow, satis.
200	60	25-27	.1008	?	Heavy TlCl ppt.
200	60	25-27	.0403	.0403	Little slow, satis.
200	40	55–57	.0403	.0404	Rapid, satisfactory
100	20	55–57	.0403	.0402	Rapid, satisfactory
200	50	57-60	.2016	.2017	Rapid, satisfactory
200	30	55–57	.3024	.3026	Heavy TlCl ppt., diss. during titrn., rapid, satis.

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as catalyst and chloroform as indicator. He stated that under ordinary conditions ceric sulfate did not react with thallous salts and that even when iodine chloride was present the theoretical factor could not be used.

[9] Willard and Young, THIS JOURNAL, 51, 149 (1929).

[10] Willard and Young, *ibid.*, 50, 1322 (1928).

electrode system was used and a thermionic voltmeter, Type DP-2, from the General Electric Company. The silver chloride electrode in 0.1 N potassium chloride was placed directly in the liquid to be titrated. The quantities of the various substances and the results are indicated in Table I. One-tenth gram of thallium required about 10 cc. of 0.1 *N* ceric sulfate.

These results show that the titration of thallous salt with ceric sulfate is quantitative and satisfactory over a wide range of conditions: (a) room temperature if a large amount of hydrochloric acid is present and if the thallium content is not too high, (b) higher temperature if the volume of hydrochloric acid used is decreased or if the thallium content is large enough to cause much thallous chloride to be precipitated by the hydrochloric acid present, (c) a variation in volume of solution, (d) a variation in amount of thallium from 0.04–0.30 g. Experiments were not carried out beyond this range in thallium content. In many of the reactions, when within 0.1 cc. of the end-point the equilibrium was reached rather slowly. A sudden break in potential was followed by a slow increase for a minute or two. A complete titration never took more than ten minutes, and with a little experience required less time. At temperatures below 60°, the end-point break amounted to 200–250 mv. per 0.02 cc. of 0.1 *N* ceric sulfate, but in titrations made above 60°, the break was decreased to 40–100 mv. The type of titration curve obtained is illustrated in Fig. 1.

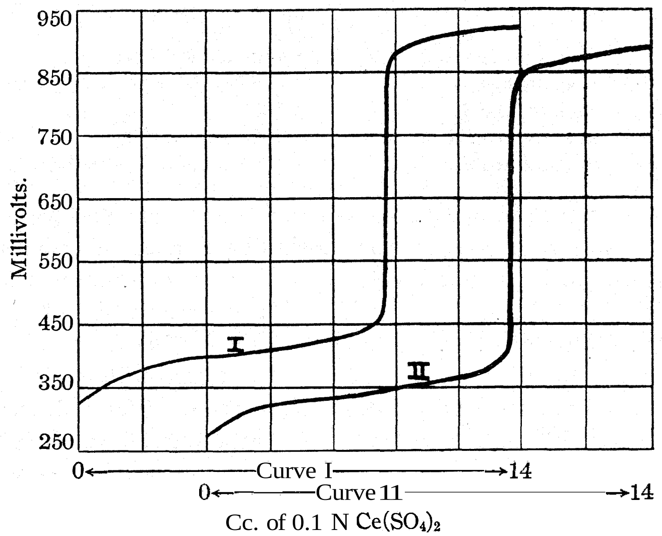

Fig. 1.—Curve I—25 cc. of Tl_2SO_4 (0.1008 g. Tl) + 145 cc. H_2O + 30 cc. concd. HCl titrated at 55–57° with 0.1 N $Ce(SO_4)_2$. Curve II—25 cc. of Tl_2SO_4 (0.1008 *g*. Tl) + 115 cc. H_2O + 60 cc. concd. HCl titrated at 34–36° with 0.1 N $Ce(SO_4)_2$.

To test this method further, the thallous sulfate solution was standardized volumetrically by the method of Zintl and Rienäcker.[6] Twenty-five cc. of the standard thallous sulfate was mixed with 165 cc. of water and 10 cc. of hydrochloric acid (sp. gr. 1-18), the solution heated to 50° and titrated electrometrically at that temperature with a standard potassium bromate solution, the oxidizing power of which had been accurately determined in this Laboratory against Bureau of Standards arsenious oxide. A comparison of the weights of thallium in 25-cc. portions of the standard thallous sulfate solution is given in Table II.

TABLE II

CONCENTRATION OF THALLOUS SULFATE SOLUTION

Method of determination	*Weight of Tl in 25 cc. of solution*
From the weight of Tl_2SO_4	0.1008
Titration with standard $KBrO_3$	0.1008 and 0.1009
Titration with standard $Ce(SO_4)_2$	0.1008 (average value from Table I)

Since in the titration of thallous salt the solution is colorless until an excess of ceric sulfate is present, the possibility of using a visual end-point was investigated. An initial volume of 200 cc. containing the amount of hydrochloric acid indicated in Table III was used, the solution heated to the given temperature and titrated without further application of heat. If an equal volume of water is taken as a comparison liquid, the slightest change in color at the end-point is easily seen. Blank determinations made at 70 and 80° on 200 cc. of water containing 20 cc. of hydrochloric acid (sp. gr. 1.18) and 3–5 cc. of sulfuric acid, sp. gr. 1.83 (since sulfuric acid is present in the ceric sulfate added), showed that 0.05 cc. of 0.1 N ceric sulfate was required to give a pale yellow color. Unless sulfuric acid was added, the ceric sulfate was reduced by the hydrochloric acid. This blank correction has been applied to the results given in Table III.

TABLE III

TITRATION OF THALLOUS SALT WITH 0.1 *N* CERIC SULFATE IN HYDROCHLORIC ACID SOLUTION. VISUAL END-POINT

HCl, *sp. gr. 1.18, present,* cc.	*Temperature,* °C. Init.	Final	Tl *taken,* g.	Tl *found,* g.	*Character of reaction*
40	55	50	0.1008	0.1008	Rapid
20	65	55	.1008	.1009	Too slow
60	35	34	.1008	.1008	Rapid
20	90	75	.1008	.1009	Very rapid
20	98	80	.1008	.1009	Very rapid

Thus it is seen that for a visual end-point the results are most satisfactory when a smaller volume of acid is used and the titration made in a very hot solution. Under these conditions the color produced by the excess ceric sulfate is more permanent.

If 5 cc. of sulfuric acid (sp. gr. 1.5) or 5 cc. of perchloric acid (70–72%) was added to a volume of 200 cc. containing 40 cc. of hydrochloric acid (sp. gr. 1.18) and thallous salt, the reaction with ceric salt was slower than in the absence of these acids, but the results were quantitative. With larger amounts of these acids the reaction was too slow. Nitric acid, even in small amounts, caused the results to be erratic. Titrations in which no hydrochloric acid was present were not possible.

The effect of the presence of various metals which occur with thallium in ores was tested. The volume of solution at the beginning of the titration was 200 cc. in every case. Results are shown in Table IV.

TABLE IV

EFFECT OF THE PRESENCE OF VARIOUS METALS ON THE VOLUMETRIC DETERMINATION OF THALLIUM

Metallic ions added, g.	HCl (sp. gr. 1.18) present, cc.	Temp. during titrn., °C.	Tl taken, g.	Tl found, g.	Character of reaction
0.5 Fe (as $FeCl_3$)	30	55–57	0.1008	0.1011	Rapid, satis.
.1 Cu (as $CuSO_4$)	30	55–57	.1008	.1008	Slightly slow, satis.
.1 Cd (as $CdCl_2$)					
.1 Bi (as $BiCl_3$)					
.1 Sn (as $SnCl_4$)					
.1 Pb (as $PbCl_2$)					
.1 Hg (as $HgCl_2$)					
.1 Zn (as $ZnCl_2$)					
.1 Cr (as $CrCl_3$)	60	34–35	.1008	.1007	Rapid, satis.
.1 Cr (as $CrCl_3$)	30	55–57	.1008	?	Results high
.1 Te (as K_2TeO_3)	60	33–35	.1008	.1007	A little slow at end-point
.1 Te (as K_2TeO_3)	30	55–57	.1008	.1010	A little slow at end-point
.1 Se (as H_2SeO_3)	60	33–35	.1008	.1006	A little slow at end-point
.1 Se (as H_2SeO_3)	30	55–57	.1008	.1008	A little slow at end-point
.1 As (as H_3AsO_4)	60	33–35	.1008	.1009	Rapid, satis.
.1 Sb (as $SbCl_5$)	60	33–35	.1008	.1007	Rapid, satis.

Thus salts of Cu^{++}, Fe^{+++}, Cd^{++}, Bi^{+++}, Sn^{4+}, Pb^{++}, Hg^{++}, Zn^{++}, SeO_3^{--}, TeO_3^{--}, AsO_4^{---}, Sb^{5+} and Cr^{+++} cause no interference in the titration of thallous ion with ceric sulfate. If Cr^{+++} is present, the acid concentration should be kept high and the temperature low to prevent any oxidation of chromium.[11] Trivalent arsenic and antimony interfere, as would be expected.[12] Zintl and Rienacker[6] in their bromate method for thallium found that Fe^{+++} caused their results to be low and erratic. They did not test the effect of selenium and tellurium, which may occur with thallium in ores.

Summary

1. Thallium may be rapidly and accurately determined by titration of thallous salt in hydrochloric acid solution with standard ceric sulfate.

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[11] Willard and Young, THIS JOURNAL, 51, 139 (1929).

[12] Willard and Young, *ibid.*, 50, 1372 (1928).

The end-point may be determined electrometrically, or visually if the solution is colorless. In the former case the titration may be made at room temperature if the concentration of hydrochloric acid present is high or at temperatures up to 60° if the concentration of hydrochloric acid is decreased. Above 60° the end-point break is usually unsatisfactory. For the visual end-point the most satisfactory conditions are low concentration of hydrochloric acid and a temperature of 80° or higher.

2. Results obtained by this method and by the bromate titration method of Zintl and Rienacker agree very closely.

3. Fe^{+++}, Cuf^{+}, Bi^{+++}, Cd^{++}, Pb^{++}, Sn^{4+}, Hg^{++}, Zn^{++}, SeO_3^{--}, TeO_3^{--}, AsO_4^{---}, Sb^{5+} and Cr^{+++} are without effect.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BUCKNELL UNIVERSITY]

THE QUANTITATIVE DETERMINATION OF OSMIUM BY MEANS OF STRYCHNINE SULFATE[1]

BY S. C. OGBURN, JR., AND L. F. MILLER

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The analytical separations of osmium and ruthenium from the other metals of the platinum group have been based largely on the volatility of their tetroxides from acid and alkaline solutions, respectively. The use of certain organic complexes in the formation of stable coördinated salts with the metals of this group is well known and in some cases they have been used to effect their quantitative removal.[2] Those of the oximes, aromatic nitrosoamines and hydroxyquinolines are especially useful in this connection with platinum and palladium, and 6-nitroquinoline has recently been added to the list as a quantitative reagent for palladium.[3]

In studying the analytical reactions of the platinum metals, one of us[2] found that when a saturated aqueous solution of strychnine sulfate was added to a slightly acidulated solution of sodium chlorosmate, a heavy canary-yellow precipitate was produced, which on settling left a clear supernatant liquid which gave no test for osmium with hydrogen sulfide on boiling, nor with thiourea—a test which will detect one part of osmium in one hundred thousand parts of solution. Following this evidence, the work upon which this paper is based was started with the view of determining whether or not this reagent could be used as a means of quantitatively separating osmium from solutions of its pure salts or from mix-

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[1] This paper is based upon a thesis submitted by L. F. Miller to the Faculty of Bucknell University in partial fulfilment of the requirements for the degree of Master of Science in Chemistry.

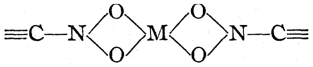
[2] Ogburn, THIS JOURNAL, 48, 2493 (1926), and other references given therein; also, Ogburn, ibid., 48, 2507 (1926).

[3] Ogburn and Riesmeyer, *ibid.*, 50, 3018 (1928).

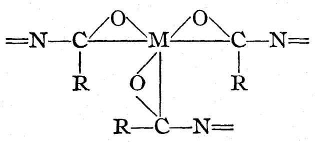
tures of osmium with the other metals of the platinum group. After some preliminary work was carried out in treating solutions of each of these metals which contained one milligram of metal per cubic centimeter of solution, it was found that in every case a precipitate was obtained with the strychnine sulfate solution. In the case of ruthenium, however, it was found that due to differences in the solubilities of the precipitate obtained with that of the osmium, in ethyl alcohol, a separation of these two metals could be effected, as will be shown later in the paper.

Although the empirical formula of strychnine, $C_{21}H_{22}O_2N_2$, is well known, its constitution is still a subject of some doubt. Perkin and Robinson[4] have stated that within the molecule there must be *a* quinoline nucleus which probably contains a benzene ring and, since carbazole is formed on reduction with zinc, there must be a carbazole nucleus.

In the case of hydroxyquinolines forming coordinated salts with metals, Bargallini and Bellucci[5] state that the condition is $\equiv C-O-M-N\equiv$ where M is one metallic equivalent and in which the ring is closed by a secondary valence. In the case of 6-nitroquinoline with palladium,[3] the structural condition is



As will be shown in this paper, the osmium salt formed with strychnine is not an additive or double salt but a true coördinated one in which the structural condition is



The stability of this salt lends itself to the quantitative separation of osmium from solutions of its pure salts, and in making use of the differences in solubility in ethyl alcohol of this salt and the corresponding ruthenium one, and in the absence of the other metals of the group, a clear cut separation is effected.

Experimental Part

Preparation of Solutions. (a) The Sodium **Chlorosmate** Solution.—Several sealed tubes containing one gram each of pure crystalline osmium tetroxide were broken beneath the surface of a 10% solution of sodium hydroxide to which sufficient ethyl alcohol was subsequently added to produce the slight reducing action necessary to cause the formation of sodium osmate. This dear rich red solution was then treated with an excess of concentrated hydrochloric acid and heated to the boiling point. This is necessary to change any osmyl chloride to the sodium chlorosmate form. This greenish to golden yellow solution was diluted, filtered into a glass-stoppered bottle

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[4] Perkin and Robinson, *J. Chem. Soc.*, 97, 309 (1910).

[5] Bargallini and Bellucci, *Gazz. chim. ital.*, 53, 605 (1923).

and kept in a cool dark place. In this form the solution is stable for several weeks, as analyses showed. Before using this solution, however, for any quantitative work it was analyzed. This analysis consisted simply in treating a known volume of the chlorosmate solution with previously determined c. p. zinc until all of the osmium was completely reduced to the metallic condition. Carefully prepared Gooch crucibles were used to contain the metal during the washing and drying operations. The analyses ran as follows

Weight of metallic osmium, g.	0.0073	0.0073	0.0072
Amount of solution used, cc.	4.0	4.0	4.0

(b) The Strychnine Sulfate Solution.—A saturated solution of this reagent was prepared at room temperature, and contained 3.2% of the salt.

Preparation of the Osmium Compound **and** the Determination of its Empirical Formula.—Approximately 135 cc. of the sodium chlorosmate solution was treated with an excess of the saturated strychnine sulfate solution. The heavy canary-yellow precipitate was immediately formed and after warming on a water-bath for a few minutes to aid in its coagulation, it was filtered through finely pored paper and washed well to remove chlorides. It was then dried in the usual manner and preserved in a desiccator. The filtrate was free from osmium, as shown by the negative tests given with such reagents as thiourea, hydrogen sulfide and zinc dust.

An analysis of the yellow compound was then made which included determinations for osmium, carbon and hydrogen. The carbon and hydrogen were determined by the usual organic combustion[6] method in which complete oxidation of the compound was attained with the formation of carbon dioxide, water and some osmium tetroxide. In the soda-lime tube of the combustion train some absorption of the volatile osmium tetroxide occurred with the formation of sodium osmate. After weighing, the quantity of osmium absorbed was determined and this amount was deducted in order to obtain the true value of carbon dioxide retained. Approximately 0.2-g. samples were used. About ten such determinations were made. Typical analyses ran as follows

Weight of sample, g.	0.1500	0.1500	0.2000	
Weight of water, g.	.0737	.0797	.0997	
Wt. of carbon dioxide, corr., g.	.3330	.3306	.4180	
Hydrogen, %	5.51	5.94	5.58	Mean value, 5.67
Carbon, %	60.54	60.10	57.00	Mean value, 59.21

The osmium content of the compound was determined by complete oxidation of the osmium in the sample and the subsequent absorption of the volatile tetroxide in 20% sodium hydroxide to which a small quantity of alcohol had been added to aid in the complete conversion to sodium osmate.

The oxidation process was carried out in an oxygen combustion train in which pure dry oxygen was slowly admitted to a transparent vitreosil combustion tube into whose outlet end was sealed, by means of asbestos cement, the entrance end of a wash bottle containing the alcoholic sodium hydroxide solution.

After prolonged preliminary heating, during which all of the volatile matter from the cement was driven off and each connection tested, the determinations were made. When all of the original sample had been completely volatilized, the temperature was maintained at a red heat for about five minutes. After cooling, the contents of the wash bottle was treated with an excess of concentrated hydrochloric acid, diluted and

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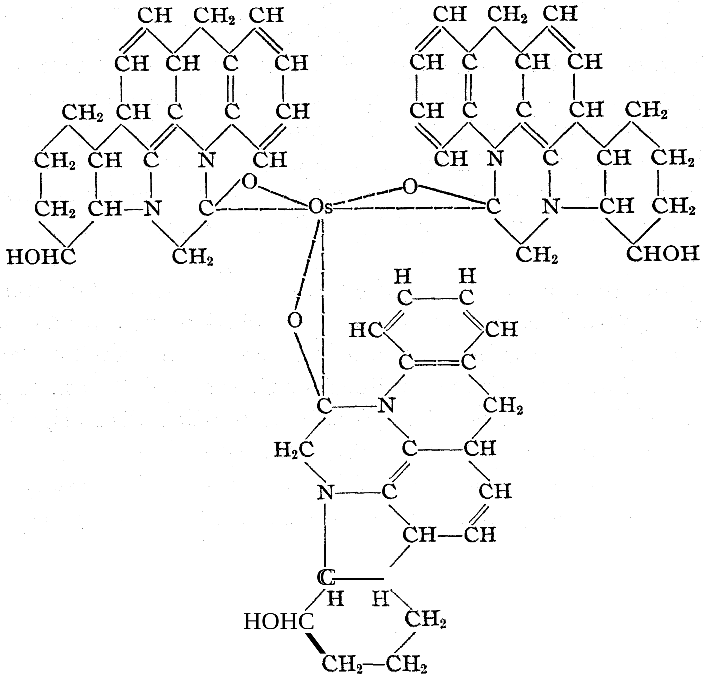
[6] See Clark, "A Handbook of Organic Analysis," 2d. ed., Edward Arnold, London, England, pp. 191–198.

treated with zinc. After complete reduction of the osmium had taken place, it was washed free from chlorides, dried and weighed. Considering the small amount of osmium in the sample taken, these determinations gave very good checks.

Weight of sample, g.	0.2000	0.2000	0.2000	
Weight of osmium recovered, g.	0.0354	0.0351	0.0350	
Oxmium, %	17.70	17.55	17.50	Mean value, 17.58

In order to ascertain whether this compound was a simple additive one, tests were made for the chloride and the sulfate ions on a solution of it in nitric acid. As neither ion was detected, the existence of a coördinated salt was indicated.

Two types of coordination were considered: the one in which the osmium replaces hydrogen and in which the ring is closed by a secondary valence as suggested by Bargallini and Bellucci in the case of hydroxyquinolines, and the other, in which the osmium links with the carbonyl group, forming a conjugated ring system shown in the fore part of this paper. This latter type of linkage is comparable with the structural condition shown in the palladium compound[3] previously described and also with Lowry's[7] study of factors influencing coordination and the use of coordination compounds in analysis. In this paper he states that "the stability of the coördination complex depends largely on the formation of a conjugated ring system in which the metallic ion M acts as a member of a pseudo-aromatic ring."



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[7] Lowry, J. Soc. *Chem. Ind.*, 42, 462 (1923).

By inspection it will be found that the mean values of the analysis of the yellow osmium compound agree rather closely with the calculated analysis of the compound $(C_{21}H_{22}O_2N_2)_3Os$ in which the osmium exhibits a coordination number of six. In this case the osmium forms a conjugated ring system with the carbonyl group of the strychnine by sharing two pairs of electrons with each three molecules of strychnine. This configuration is represented graphically as indicated.

The osmium atom, with an atomic number of seventy-six, contains two, plus eight, plus eight, plus eighteen, plus eighteen, plus twenty-two electrons in the successive shells. The tetravalent osmium ion, as in the salt sodium chlorosmate used, therefore, contains eighteen electrons in the outer shell, and requires fourteen more to complete the shell of thirty-two. By drawing into this shell one pair of electrons in each of three atoms of oxygen and three atoms of carbon, the osmium coordination number of six is satisfied but there remains a deficiency of two electrons to complete the outer shell, thus rendering the compound stable to the maximum extent. This deficiency, however, is permissible with the formation of stable salts as ascertained by Lowry[8] in which he states that "this shortage of electrons is, however, tolerated much more readily than a surplus as is indeed indicated by the fact that a shortage of three, two and one electrons, respectively, is found in the coordinated compounds, $K_3(Cr{\cdot}6CN)$, $K_2(Pt{\cdot}4CN)$ and $K_3(Fe{\cdot}6CN)$."

The Removal of Osmium from a Solution of Sodium Chlorosmate.—After having determined from the analysis of the yellow osmium compound the gravimetric factor of 0.1758 for its osmium content, a series of analyses was made of sodium chlorosmate solutions of known osmium content, to check the accuracy of this factor and to show the ease with which the reagent, strychnine sulfate, could be used for the quantitative estimation of this metal.

The previously prepared osmium solution, having stood for about forty-five days, was slightly decomposed. The solution was filtered and the osmium content determined by means of zinc reduction as previously described. Close checks were obtained for the value 0.0014 g. of osmium per cubic centimeter of solution. It will be recalled that originally this solution analyzed 0.0018 *g.* per cubic centimeter.

Five cubic centimeter portions of this chlorosmate solution were treated with an excess of strychnine sulfate solution and the resulting canary-yellow compound filtered. After carefully washing with distilled water until free from chlorides, it was dried to 105° in an electric oven, cooled and weighed. The results of three such determinations were found to coincide with the theoretical weight of the precipitate as calculated by use of the gravimetric factor mentioned above.

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[8] Lowry, *J. Soc. Chem. Ind.*, **42**, 316 (1923).

	Soln. boiled during pptn.		Soln. pptd. cold.
Sodium chlorosmate used, cc.	5.0	5.0	5.0
Osmium per cc., g.	0.0014	0.0014	0.0014
Total osmium in soln., g.	.0070	.0070	.0070
Actual wt. of osmium ppt., g.	.0402	.0406	.0399
Theoretical wt. of ppt., g.	.0400	.0400	.0400

From these data it is conclusively shown that osmium may be quantitatively removed from solutions of its salts by means of a saturated solution of strychnine sulfate, and by use of the gravimetric factor 0.1758 the percentage of osmium in the original sample may be calculated from the weight of the washed and dried canary-yellow precipitate obtained. It is also shown that the solubility of the precipitate in water up to its boiling point is negligible. Following the preceding work, a 0.0400-g. sample of the precipitate was allowed to stand overnight in 20 cc. of distilled water at room temperature. On analyzing this solution for osmium by the nascent hydrogen reduction method (zinc and hydrochloric acid) no trace of osmium was found. The thiourea test also failed to detect any metal.

The Separation of Osmium from Ruthenium.—Strychnine sulfate gives with a slightly acidulated solution of ruthenium trichloride a yellow precipitate which is partially soluble on boiling. In no case is this precipitation complete. In the experimental work on the separation of the precipitates obtained by the use of this reagent on solutions containing both osmium and ruthenium, numerous solvents were tried under varying conditions in an effort to effect a complete separation of the osmium compound. Of these, ethyl alcohol was found effective as a means to this end.

A solution containing 0.0014 g. of osmium and 0.0016 g. of ruthenium in soluble form (sodium chlorosmate and ruthenium trichloride) was treated with a small excess of the saturated solution of strychnine sulfate. Immediate precipitation followed. An equal volume of 95% ethyl alcohol was then added and the mixture boiled until the precipitates dissolved. Upon cooling, the osmium compound reprecipitated and after standing for one and one-half hours, it was filtered.[9] The filtrate gave no test for osmium with β-naphthalamine hydrochloride.[10] The results of these determinations were:

Weight of osmium, g.	0 0014	0 0014
Weight of osmium precipitate, g.	.0076	.0078
Theoretical weight of precipitate, g.	.0080	.0080

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[9] Preliminary tests showed no contamination of this precipitate by the ruthenium compound. The latter remained in solution, on cooling, for a period of several days.

[10] The test with thiourea or other usual reagents for osmium cannot be used in the presence of ruthenium. The blue color produced by the reaction of the β-naphthylamine hydrochloride with osmium is a delicate and characteristic test which can be used in the presence of ruthenium. See Ref. 2.

Due to the small quantities of metals used, these small deviations may be regarded as within the limits of experimental error. Such determinations show that osmium may be removed quantitatively from a mixture containing one of its salts with that of ruthenium by means of strychnine sulfate.

Summary

A new quantitative method for the determination of osmium is given. The metal is removed from a solution of sodium chlorosmate by means of a saturated aqueous solution of strychnine sulfate. The composition of the compound formed was found to be $(C_{21}H_{22}O_2N_2)_3Os$, a coordinated salt in which osmium exhibits a coordination number of six. By use of the gravimetric factor, 0.1758, the percentage content of the osmium may be obtained from a direct weighing of the canary-yellow precipitate.

Strychnine sulfate reacts with the formation of precipitates with all of the platinum metals, but the precipitate formed with ruthenium is soluble in boiling ethyl alcohol, from which it does not easily separate on cooling even after a period of several days. This method may be used in effecting a separation of osmium from ruthenium since the former compound reprecipitates completely on cooling the alcoholic solution.

LEWISBURG, PENNSYLVANIA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 224]

THE HIGH-TEMPERATURE EQUILIBRIUM BETWEEN SILICON NITRIDE, SILICON AND NITROGEN

BY W. B. HINCKE AND L. R. BRANTLEY

RECEIVED JULY 6, 1929 PUBLISHED JANUARY 8, 1930

Plan of the Investigation

This investigation is a continuation of the researches in progress in this Laboratory on high-temperature equilibria.[1] The method devised by Prescott and used by Prescott and Hincke[1d] in studying the equilibrium of the system aluminum carbide, nitrogen, aluminum nitride and carbon was employed. This method consists in heating by an electric current to various temperatures (measured by an optical pyrometer) the solid reaction mixture (in this case the silicon nitride and silicon) within a graphite tube a few millimeters in diameter and a few centimeters long placed within a pyrex bulb, and in measuring the pressures produced. In this article are described measurements made of the dissociation pressures of silicon nitride from 0.27 to 5.49 mm. through a temperature range from 1606 to 1802°K.

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[1] (a) Prescott, THIS JOURNAL, 48, 2534 (1926); (b) Prescott and Hincke, *ibid.*, 49, 2744 (1927); (c) Prescott and Hincke, *ibid.*, 49, 2753 (1927); (d) Prescott and Hincke *ibid.*, 50, 3228 (1928); (e) Prescott, *ibid.*, 50, 3237 (1928); (f) Prescott and Hincke, *Phys. Rev.*, 31, 130 (1928).

It has been shown by Weiss and Engelhardt[2] and by Funk[3] that the compound produced, when silicon is heated in nitrogen at 1300 to 1450° as long as the gas continues to be absorbed, is the normal nitride, Si_3N_4. The nitride produced in the experiments here described presumably had this composition, since the conditions of heating were substantially the same.

The authors wish to express their thanks to Dr. C. H. Prescott, Jr., whose suggestions and criticisms have been of great assistance.

Apparatus and Procedure

The temperature measurements in this investigation were made by means of an optical pyrometer with a disappearing filament; the details, corrections and limitations of these measurements have already been described.[1b,f] The furnace, the devices for introducing nitrogen and the McLeod gages have also been described.[1d]

The silicon used was a C. P. Eimer and Amend preparation which had been ground to pass a 200-mesh sieve. The preparation upon treatment with hydrofluoric and nitric acids, evaporation with nitric acid and ignition of the residue yielded 2% of oxides, corresponding to about 1% of metallic impurity.

In the procedure adopted there was placed loosely in the middle zone of the graphite tube a charge of 0.1 g. of finely powdered silicon. After complete evacuation, the apparatus was filled at one atmosphere with (tank) nitrogen that had been passed through a purifying train, and the furnace was heated to 1675°K. for thirty minutes. This converted about 75% of the charge to silicon nitride.[4] The apparatus was then evacuated, after which it was ready for the equilibrium measurements.

In all of the determinations the temperature of the furnace was held constant, and the equilibrium pressure was found by taking the mean of the final pressures of a forward and a reverse reaction wherein the pressure in the glass bulb containing the graphite furnace increased and decreased, respectively. To hold the furnace at a constant temperature it sufficed to keep the current through it constant, which was done by means of a standard resistance and a potentiometer. A shower of tap water was caused to play continuously over the glass bulb containing the graphite tube while equilibrium measurements were being made. This prevented excessive outgassing of the glass walls and contamination of the nitrogen. A gas micro-analysis apparatus[1d] was used to determine the partial pressure of nitrogen at the end of each experiment. In all the satisfactory runs the nitrogen formed more than 92% of the gases in the bulb.

For the preliminary formation of silicon nitride the current was drawn from a 1-kilowatt transformer. During the measurements it was taken from storage batteries. To maintain the furnace at 1802°K. about 80 amperes at 10 volts was required.

The Equilibrium Measurements

The first equilibrium determination was made at **1675°K.** The pressure of the nitrogen in the bulb built up from a vacuum to **0.47** mm. in the course of one hour, the gas then containing 92% of nitrogen. The apparatus was then again evacuated and filled to 0.90 mm. of nitrogen, as measured when the furnace had become hot; in this case the pressure of the gas decreased

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[2] Weiss and Engelhardt, *Z. anorg. Chem.*, 65, **78** (1910).

[3] Funk, *ibid.*, **133,** 67 (1924).

[4] No silicon carbide was formed at this nitrogen pressure by the reaction of silicon with the graphite furnace; moreover, it was found that silicon carbide is inert to nitrogen under the conditions of these experiments.

in one hour to 0.762 mm., and the gas contained 95% of nitrogen. Two one-hour runs were then made, one at 0.57 mm. and the other at 0.675 mm. of nitrogen, but these showed no measurable change in pressure. Finally a run of two hours with increasing pressure was made, starting from an initial pressure of 0.336 mm. and stopping at 0.553 mm. of nitrogen. The gas analysis showed 100% of nitrogen in this run, which was to be expected because of the pumping off of the outgassed impurities in the previous runs. It was observed that a pellet reacted more slowly after some hours of heating, probably owing to loss of some of the silicon from the charge by volatilization and to sintering of the silicon nitride into a more compact mass.

The pellets removed from the furnaces after each equilibrium determination always gave the characteristic ammonia test on heating with concentrated alkali, and under a low powered microscope showed a white sintered mass speckled with darker particles of silicon.

In each determination the true equilibrium pressure of the nitrogen corresponding to any temperature was assumed to be the average of the two pressures which had been attained in a forward and a reverse run. Each of the two pressures always approached a limiting value that seemed to be as far as the reaction would go within a reasonable time. These pressures, however, did not differ very greatly from one another. At temperatures above 1800°K. sublimation of the silicon and sintering of the silicon nitride were so rapid that a pellet became only slowly reactive after a few runs. This permitted, nevertheless, a range of about 200° over which the equilibrium could be studied.

Table I gives the final pressures (in millimeters) observed at each temperature. There are shown in each case the highest pressures (marked "increasing") which were attained by the forward reaction (decomposition of the nitride) and the lowest pressures (marked "decreasing") which were attained by the reverse reaction. These pressures are always the partial pressure of the nitrogen in the gas (found by multiplying the total pressure by the fraction of nitrogen present). The mean values of these two pressures for each pair are taken as the equilibrium pressures. The correspond-

TABLE I

EQUILIBRIUM PRESSURES OF THE REACTION AT VARIOUS TEMPERATURES AND THE CORRESPONDING FREE ENERGIES

Absolute temp., T	$10^4/T$	Final pressure in mm.			Pressure $\times 10^4$ in atm.	Free energy, A P
		Increasing	Decreasing	Mean		
1606	6.225	0.179	0.361	0.27	3.5	50,800
1638	6.110	.382	.537	.46	6.0	48,300
1675	5.971	.553	.762	.66	8.7	46,900
1709	5.850	1.110	1.335	1.22	16.1	43,700
1739	5.750	2.215	2.675	2.44	32.0	39,700
1779	5 625	3 560	4.65	4.11	54.0	36,900
1802	5.550	5.05	5 93	5.49	72.0	35,300

ing values expressed in atmospheres are given in an adjoining column. In the last column of the table are given also the values (derived as described below) in calories of the free-energy increase (AF) attending the reaction $Si_3N_4(s) = 3Si(s)$ or (1) $+ 2N_2(g)$.

In Fig. 1 are plotted as full circles the mean values of $\log_{10} p$ (in mm.) against $10^4/T$. The straight line was drawn so as to fit best the full circles. The corresponding observed "increasing" and "decreasing" values are shown by half-circles.

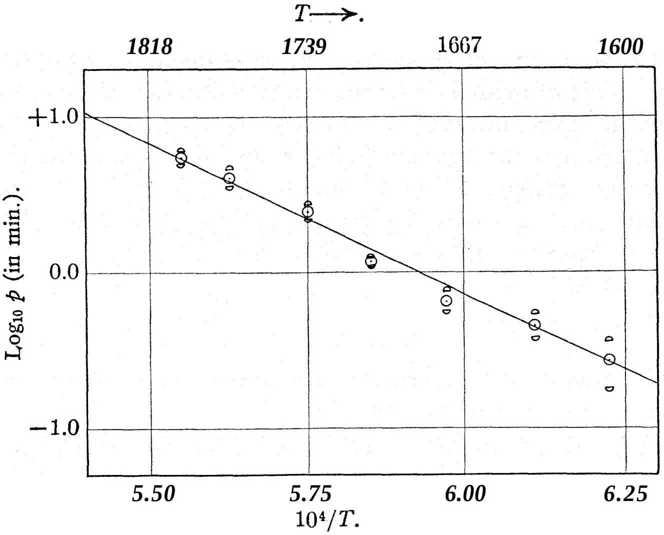

Fig. 1.

The final relation between the equilibrium pressures in atmospheres and the absolute temperature is given by the equation

$$2.3 \log_{10} p \text{ (in atm.)} = 19.75 - \frac{44,500}{T}$$

Since the melting point of silicon is approximately 1687°K., there should be a slight change in slope of the line at this temperature due to the heat of fusion of the silicon, but the data are not accurate enough to show this change in slope.

Thermodynamic Calculations

The chemical reaction is $Si_3N_4 = 3Si + 2N_2$. The free-energy increase (ΔF) attending it when the nitrogen pressure is one atmosphere may then be derived from the equilibrium pressure p in atmospheres by the familiar equation $\Delta F = -RT \ln K$, where $K = p^2$ and $R = 1.987$. From the determinations of the equilibrium pressure p are thus obtained the values of A F given in the last column of Table I.

From these values of the free-energy increase one obtains the function

AF = 176,300 − 78.35*T* for absolute temperatures between 1600 and 1800°. From this it follows that the heat-content increase A H is 176,300 calories in this temperature range. The function shows also that at an absolute temperature of 2250° (assuming it to hold up to this temperature) the free-energy increase becomes zero and therefore that the dissociation pressure becomes one atmosphere at this temperature.

Summary

The pressure of nitrogen at which equilibrium prevails between silicon nitride, Si_3N_4, and its elements at absolute temperatures ranging from 1606 to 1802°K. has been determined by an experimental method previously described. This pressure is 0.27 mm. at 1606°K. and 5.5 mm. at 1802°K. Within this temperature interval the free-energy increase *AF* at one atmosphere attending the reaction $Si_3N_4 = 3Si + 2N_2$ was found to be expressed by the function *AF* = 176,300 − 78.35 T calories. From this it follows that the heat-content increase ΔH at 1700°K. is 176,300 cal.; **also** that the dissociation pressure of the nitride becomes one atmosphere at about 2250°K.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 225]

THE RATE OF REACTION IN A CHANGING ENVIRONMENT

BY GEORGE SCATCHARD

RECEIVED JULY 10, 1929 PUBLISHED JANUARY 8, 1930

In the study of the reaction rates described in the following paper[1] there were developed methods which are of general applicability to the treatment of rates in non-ideal solutions in which the deviations change during the course of the reaction. Graphical methods applicable to this problem were presented in an earlier paper;[2] the present method is analytical and therefore much easier to apply. Although approximate, it is in most cases as accurate as the rate measurements.

The treatment is based upon the theory of Bronsted[3] that the mechanism of the reaction is the formation and decomposition of a "critical complex," so that for the simple bimolecular reaction

$$A + B \rightleftharpoons X(= AB) \longrightarrow D + E$$

the rate is given by

$$-\frac{dC_A}{dt} = KC_AC_B\frac{f_Af_B}{f_X} \tag{1}$$

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[1] Ashdown, THIS JOURNAL, 52,268 (1930).

[2] Scatchard, *ibid.*, 48,2259 (1926).

[3] Bronsted, *Z. physik.* Chem., 102,169 (1922), and many later papers. The method is more general than this theory, however. For example, it may be applied to the simple activity theory merely by replacing f_X by 1.

where C represents concentration and f activity coefficient. It makes no difference, except for convenience, whether the concentrations are expressed as mole fractions, or weight or volume concentrations, for the units of the C and f terms cancel.[4] The rate expression should contain the concentration and activity coefficient of every molecule which enters into the complex, whether it be reactant, catalyst or solvent. If the reaction may proceed by more than one mechanism, there should be a term on the right-hand side, each with its own value of K, for each critical complex formed. It is certain that those reactions proceed by more than one mechanism which occur both with and without a catalyst, or with two different catalysts. It is probable that the phenomenon is much more general. The fact that the effect of changing solvent on the rate is much larger than the change of activities of the reactants, so much larger that it is extremely improbable that any change in the activity coefficient of a critical complex can explain it, is most simply accounted for by assuming that the solvents enter into the complexes, so that the mechanism is not the same in different solvents.

Dilute Electrolytes.—Except from the rate measurements themselves, the activity coefficient of the critical complex can be determined only for electrolyte solutions so dilute that the activity coefficient of an ion depends only upon its valence. The Debye–Hückel expression for the activity coefficient of an ion in water at 25° is

$$-\ln f_i = \frac{1.16 z_i^2 \sqrt{\mu}}{1 + 0.328 a \sqrt{\mu}} \qquad (2)$$

where f_i is the activity coefficient, z_i the valence of the ion, negative for a negative ion, and μ is the ionic strength in moles per liter. The numerical constants vary with the temperature and the dielectric constant of the solvent, a is the apparent diameter of the ion in Ångström units, and is generally between 0 and 5. In very dilute solutions it may be neglected to give the Debye–Hückel limiting law.

If the same size be attributed to all the ions

$$\ln \frac{f_A f_B}{f_X} = \frac{-1.16 \sqrt{\mu}}{1 + 0.328 a \sqrt{\mu}} [z_A^2 + z_B^2 - (z_A + z_B)^2] = \frac{2.32 z_A z_B \sqrt{\mu}}{1 + 0.328 a \sqrt{\mu}} \qquad (3)^5$$

For a more complicated complex, the valence term, $z_A z_B$, is replaced by the sum of all the cross products of the z's. This equation shows immediately the conclusions drawn by Bronsted that the rate should have no primary salt effect for a reaction between an ion and a neutral molecule, that the rate should increase with increasing salt concentration for reac-

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[4] The equation may be written so that the f and C terms occur only as products, f C (f_X and dC_A occurring together), which, like activities, are ratios and so pure numbers. The numerical value of K does depend on the conventional definition of unit activity.

[5] A similar expression using the Debye–Hiickel limiting law is given by Brönsted and Livingstone, THIS JOURNAL, 49, 435 (1927).

tions between two ions of the same sign, and should decrease for reactions between ions of opposite signs. Within the range of its applicability it gives quantitatively the magnitude of these changes. Bronsted's application is limited to reactions where the ionic strength and therefore the activity coefficients are constant during the course of the reaction.

When the ionic strength varies, the use of Equation **3** introduces a variable exponential which leads to difficulty in integration. The activity of an ion may also be expressed by

$$f_i = \frac{1}{1 + 1.16x_i^2\sqrt{\mu}} \qquad (4)^6$$

For small values of $z_i^2\sqrt{\mu}$, Equation 4 gives the same result as Equation **3,** with $a = 1.77z_i^2$. The corresponding value of a decreases slowly with increasing concentration, becoming 1.54 when $z_i^2\sqrt{\mu}$ is 1. This expression represents the data as well as any which does not introduce specific constants.

Then

$$\frac{f_A f_B}{f_X} = \frac{1}{1 - 2.32z_A z_B\sqrt{\mu}} \text{ when } z_A z_B \text{ is negative, and} \qquad (5a)$$

$$\frac{f_A f_B}{f_X} = 1 + 2.32z_A z_B\sqrt{\mu} \text{ when } z_A z_B \text{ is positive} \qquad (5b)$$

Since the ionic strength is a linear function of the extent of the reaction, it can be expressed as $\sqrt{\mu} = \sqrt{\mu_0}\sqrt{1 + gx}$, where x is the extent of the reaction, μ_0 is the initial ionic strength, and $\mu_0(1 + g)$ is the ionic strength when the reaction is complete $(x = 1)$. Simplification in integration without significant loss in accuracy may be obtained by replacing $\sqrt{1 + gx}$ by $1 + gx/2$. The difference between the two expressions is less than 10% even when the ionic strength is doubled or halved.

Not many reactions have been studied with a large change in ionic strength and without complicating factors such as the formation of unknown amounts of complex ions or of weak electrolytes. The studies of Yost[7] on the oxidation of ammonia by persulfate ion indicate that the slow reaction is

$$S_2O_8^{=} + Ag(NH_3)_2^{+} \longrightarrow 2SO_4^{=} + Ag^{+++} + 2NH_3$$

Since the complex silver ion is regenerated in the subsequent rapid reaction, the reaction is apparently unimolecular, and $z_A z_B = -2$. The expression for the rate is then

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[6] Two ways of expressing Equation 2 as a power series are

$$f_i = 1 - 1.16\,z_i^2\sqrt{\mu} + (0.673\,z_i^4 + 0.380\,z_i^2a)\mu + \dots\dots$$
$$1/f = 1 + 1.16\,z_i^2\sqrt{\mu} + (0.673\,z_i^4 - 0.380\,z_i^2a)\mu + \dots\dots$$

Since a is positive the two coefficients of μ compensate in the second expression, but add in the first. This is true also in the higher terms, so the first two terms of the second expression (Equation 4) give a much more accurate expression of Equation 2 than the corresponding terms of the first.

[7] Yost, THIS JOURNAL, 48, 374 (1926).

$$\frac{dx}{dt} = KC_{Ag}(1 - x)\frac{f_A f_B}{f_X} = \frac{KC_{Ag}(1 - x)}{1 + 4.64\sqrt{\mu_0}\sqrt{1 + gx}}$$

$$\frac{dx}{1 - x}(1 + 4.64\sqrt{\mu_0}\sqrt{1 + gx}) = KC_{Ag}dt \qquad (6)$$

or, approximately

$$\frac{dx}{1 - x}[1 + 4.64\sqrt{\mu_0}(1 + gx/2)] = KC_{Ag}dt \qquad (7)$$

Integrating between the limits t = 0 and $t = t$ gives, in the two cases

$$\ln\frac{1}{1 - x} + 4.64\sqrt{\mu_0}\left[\sqrt{1 + g}\ln\frac{(\sqrt{1 + g} + \sqrt{1 + gx})(\sqrt{1 + g} - 1)}{(\sqrt{1 + g} - \sqrt{1 + gx})(\sqrt{1 + g} + 1)} - 2(\sqrt{1 + gx} - 1)\right] = KC_{Ag}t \qquad (8)$$

$$[1 + 4.64\sqrt{\mu_0}(1 + g/2)]\ln\frac{1}{1 - x} - 2.32g\sqrt{\mu_0}\,x = KC_{Ag}t \qquad (9)$$

Neglecting the change of environment during the reaction (putting $g = 0$), gives

$$(1 + 4.64\sqrt{\mu_0})\ln\frac{1}{1 - x} = KC_{Ag}t \qquad (10)$$

Table I shows the application of these equations to two measurements of Yost starting with 0.0138 *M* $(NH_4)_2S_2O_8$ and 0.0059 M $AgClO_4$. The initial ammonia concentrations are 0.0687 *M* and 0.1123 M. The ionic strength changes from 0.0473 to 0.0887, so that $g = 0.875$. The first column gives the time, the second the fraction of persulfate ion converted, and the last three columns give the values of the constants computed by Equations 10, 8 and 9. Comparison of the last two columns shows that the error introduced by the approximation of Equation 7 is negligible. By Equation 10 or by the ideal solution law the constant decreases about 20%. By either of the other two equations there is no trend up to 90% conversion. As shown by the figures in parentheses, the decrease beyond this point may be prevented by decreasing the observed values of the persulfate-ion concentration by one unit in the last place given, which should be within the experimental error.

TABLE I

OXIDATION OF AMMONIA BY PERSULFATE ION

$NH_3 = 0.0687$ M					$NH_3 = 0.1123$ M				
Time	x	$K_{(10)}$	$K_{(8)}$	$K_{(9)}$	Time	x	$K_{(10)}$	$K_{(8)}$	$K_{(9)}$
5.5	0.18	12.4	12.6	12.6	5	0.22	16.7	17.1	17.1
15.5	.41	11.7	12.3	12.3	17	.54	15.4	16.4	16.4
26	.59	11.8	12.7	12.7	26	.70	15.6	16.9	17.0
40	.73	11.2	12.2	12.3	39.5	.83	15.1	16.7	16.8
57	.84	11.0	12.2	12.3	57.5	.91	14.5	16.2	16.5
91	.94	10.2	11.5	11.7 (12.2)	91	.97	13.2	15.2	15.4 (16.6)
125	.97	0.95	11.0	11.3 (12.1)	125	.99	11.6	13.5	13.6 (15.9)

It is possible, however, that this decrease is due to the fact that Equation 5 gives too small a correction for the changing activity coefficients in this case. Yost found that with 0.0086 M $K_2S_2O_8$, 0.005 M $AgClO_4$ and 0.383 M NH_3, a change in KOH concentration from 0.0170 *M* to 0.0904 M decreased K by 32%. According to Equation 5 the decrease should be 23%, while according to the Debye–Hückel limiting law it should be 45%.

The measurements of King[8] on the same reaction are affected by some disturbing factor at the start. Integrated from the first reading rather than from zero time, however, Equations 8 or 9 give values of K without a trend.

Non-Electrolytes,—There are in the literature descriptions of many reactions between non-electrolytes whose rates change during the course of the reaction, so that they do not give constants for a reaction of any order. Although the term $f_A f_B / f_X$, or its equivalent for reactions of other types, cannot be determined independently, an approximate expression can be derived so that it may be determined from the rate measurements themselves.

The activity coefficient of a non-electrolyte in dilute solution in another non-electrolyte may be expressed by

$$\ln f_1 = gm_1 \text{ or } f_1 = e^{gm_1} \qquad (11)$$

in which m_1 is the molality and g a constant.[9] Where gm_1 is large, this gives only a very rough approximation. As for the electrolyte solutions, we will substitute an expression which is the same as (11) for small values of gm_1, and which for larger values agrees as well with the experimental data.

$$-\ln f_1 = \ln (1 - gm_1) \quad 1/f_1 = 1 - gm_1 \qquad (12)^{10}$$

Figure 1 shows the values of the activity coefficients, $f = a/m$, for *iso*-amyl alcohol and for propionic acid in dry nitrobenzene, two examples of very large deviations, computed by Brown and Bury[11] from their freezing point measurements. The broken lines are for Equation 11 and the full lines for Equation 12, the constants in both cases being selected to give agreement at 1 M. For the alcohol the agreement of the two equations

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[8] King, THIS JOURNAL, 49, 2689 (1927). Dr. King has been kind enough to send me the manuscript of his article with Mr. F. I,. Griswold which indicates that under these conditions the reaction does not go quantitatively to nitrogen but part of the ammonia is oxidized to nitrate ion. We are agreed that this finding has no effect on the conclusions of this paper. The constants should be increased, but not more than 0.2%.

[9] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 275. In their notation, $g = -2h$.

[10] Equation 12 may be derived from Equation 11 by expansion of $1/f_1$ as a power series.

[11] Brown and Bury, J. Phys. Chem., 30, 696 (1926). The values there tabulated are the activity divided by the mole fraction.

is about the same. For the acid, Equation 12 fits much better, although still only fairly well.

The reaction mixtures are not binary, however, and a term must be added to our expression to include every substance whose concentration varies, giving for our type reaction

$$1/f_A = 1 - g_{AA}m_A - g_{BA}m_B - g_{DA}m_D - g_{EA}m_E \qquad (13)$$

Since the concentration of each substance is a linear function of the extent of the reaction, we may write

$$1/f = 1 - G_A - G'_A x \qquad (14)$$

where G_A and G'_A are functions of the initial composition of the solution. If the ratios of the concentrations are constant, the G's are proportional to the concentrations. Equation 14 with similar expressions for f_B and f_X permits integration, but it is generally desirable to simplify first by ignoring relatively small terms in Equation 13.

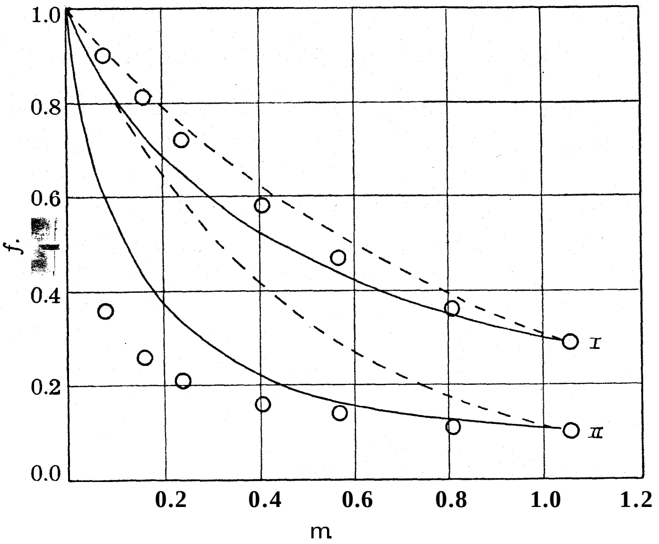

Fig. 1.—Activity coefficients in dry nitrobenzene: I, iso-amyl alcohol, g=1.17 (Eq. 11), = 2.32 (Eq. 12); II, propionic acid, g=2.18, 8.51.

The Magnitude of the Deviations.—The value of g in Equation 11 or 12 is closely related to the change of activity of the solute as the medium changes from pure solute to pure solvent. This may be seen by expanding Margules' equation in terms of activities instead of partial pressures[12]

$$RT\ln\frac{f}{f_0} = \frac{\beta}{2}(1-N)^2 + \frac{\gamma}{3}(1-N)^3 = \left(\frac{\beta}{2}+\frac{\gamma}{3}\right) - (\beta+\gamma)N + \left(\frac{\beta}{2}+\gamma\right)N^2 - \frac{\gamma N^3}{3} \qquad (15)$$

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[12] See Hildebrand, "Solubility," Chemical Catalog Co., Inc., New York, 1924, p. 48.

In this equation N is the mole fraction, and f the activity divided by the mole fraction; β and γ are constants; f_0 is the activity coefficient of the pure substance. When $N = 0$, $f = 1$ and $\ln f = 0$, so

$$RT \ln 1/f_0 = \left(\frac{\beta}{2} + \frac{\gamma}{3}\right)$$

$$RT \ln f = -(\beta + \gamma)N + \left(\frac{\beta}{2} + \gamma\right)N^2 - \frac{\gamma N^3}{3} \qquad (16)$$

For dilute solutions we may neglect the terms in N^2 and N^3 and replace the mole fraction by the concentration in moles per thousand grams of solvent or per liter of solution, with the appropriate change of constant. For the former this gives Equation 11. The neglected terms give deviations in the same direction as does Equation 12.

For binary mixtures it is possible to predict the value of $g_{11} = \frac{-N(\beta + \gamma)}{mRT}$ by the methods of Hildebrand or of Mortimer.[13] For mixtures of two non-polar substances, for which the γ term in Equation 15 is generally small, these methods are quite precise. For one non-polar and one polar component they are only approximate. For both these cases g_{11} is negative. For mixtures of two polar substances these methods may fail completely because such mixtures have a tendency to chemical reaction. If there is chemical combination between the solute and the solvent g_{11} is positive, but Equation 12 still holds approximately.

If a second solute forming an ideal solution in binary mixture with the solvent ($g_{22} = 0$) is added to a solution containing a non-ideal solute, its effect will be the same as diluting with the solvent and $g_{21} = -\frac{n_1}{n_0}g_{11}$, where n_1/n_0 is the mole ratio of the first solute to the solvent. For dilute solutions g_{21} will be small relative to g_{11}. Moreover, $g_{12} = g_{21}$. This is most simply obtained from the expression, given by Bjerrum,[14] $\frac{d \ln f_1}{dn_2} = \frac{d \ln f_2}{dn_1}$, but it may also be obtained from the fact that the change must be the same for the ideal solute as for the solvent.

If there is a third solute which forms an ideal solution with the first, and so does not with the solvent, $g_{31} = g_{13} = g_{11} = g_{33}$, and, of course, $g_{32} = g_{23} = g_{12} = g_{21}$.

If the added solute does not form an ideal solution with either the solvent or the first solute, there are two possibilities. If the solution is intermediate in its properties between the two solutes, $g_{41} = g_{14}$ will be positive; if it is not, $g_{41} = g_{14}$ will be negative and will lie between g_{11} and g_{44}. There is then a possibility that g_{41} may change sign with changing concen-

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[13] See Hildebrand, Ref. 12, pp. 99–116.

[14] Bjerrum, Z. physik. Chem., **104**, 423 (1923).

tration instead of remaining constant, but it is improbable that this should happen in dilute solution unless g_{41} is always small enough to be negligible.

If two of the components are polar, the situation may be very considerably complicated. If the two solutes react together their effect on each other may be very much greater than that of either on itself. If either or both react with the solvent, it may be very much less.

It is possible to make some tentative conclusions regarding the effect of changing environment on the activity coefficient of the critical complex. Since the complex formation may be assumed to involve the more active groups, and therefore to screen them, the complex may be taken as less polar than its most polar component, and possibly less polar than either. If the complex also contains solvent molecules, which is probably quite often the case, it may be a more ideal solute than any of its components other than the solvent. This term will tend to make the deviations from ideality less than would be predicted from the simple activity theory.

Illustration.—As an example of the application of the method we may take the action of *p*-nitrobenzoyl chloride with some of the simpler alcohols in ether solution, which is considered in detail in a paper which follows.' Not many ether solutions have been studied accurately, but the freezing points of benzene from solutions of ether are almost identical with those from solutions of toluene, which are known to be nearly ideal. Therefore ether may be taken as not much different from benzene as a solvent. Figure 2 shows the freezing-point curves of ether, toluene, benzoyl chloride and propyl alcohol in benzene.[15] The freezing points of solutions of ethyl acetoacetate[16] are identical with those of ether or toluene up to 1 molal (the limits of the measurements), so the esters should behave as ideal solutes and have little effect on the activity coefficients of the other solutes. Benzoyl chloride does not differ very greatly from the ideal solutes, so we may assume, with considerable probability, that the activity coefficient of nitrobenzoyl chloride is near unity and equal to that of the critical complex. The acid chloride should also have little effect on the activity coefficient of the alcohol. The alcohols, however, should show large deviations depending largely on their own concentration. The hydrogen chloride formed in the reaction shows a great tendency to chemical combination; it forms stable compounds with ether. Its effect on the activity coefficients appears to depend upon its relative reactivity with the solute and with the solvent, which is most easily determined from the rate measurements themselves. For hutyl alcohol the rate was found to be unchanged when one mole of hydrogen chloride was added to one mole of alcohol and one of chloride in a thousand grams of ether. Further confirmation was obtained from the fact that the curves

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[15] "International Critical Tables," Vol. 4, pp. 112, 116, 177,

[16] Auwers, *Z. physik. Chem.*, **12,693 (1893).**

for initial concentrations of one molal and of one-half molal fit together smoothly as functions of the alcohol concentration, showing that one-half mole of hydrogen chloride plus one-half of ester have no effect on the rate. So only the change of the activity coefficient of the alcohol due to changes in its own concentration need be considered. The higher alcohols behave as does butyl. Not enough measurements were made on propyl alcohol to determine the effect of the hydrogen chloride.

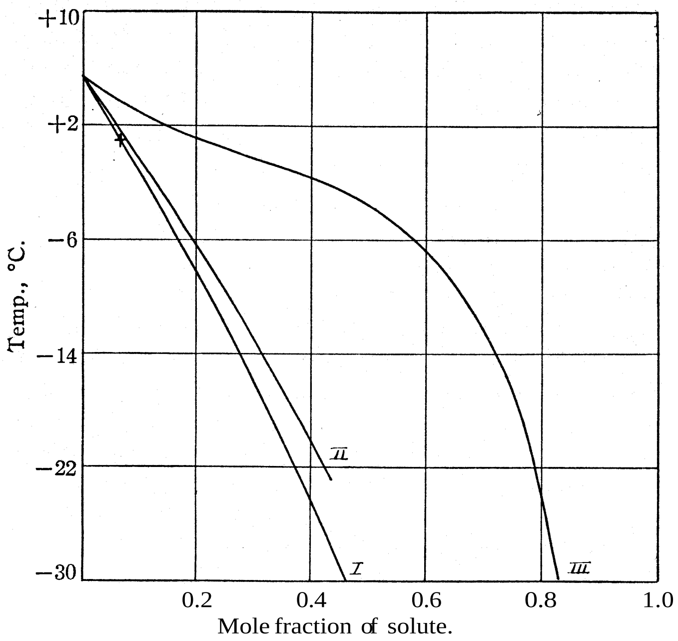

Fig. 2.—Freezing points of benzene solutions: I, toluene, ether; ethyl acetoacetate to +; II, benzoyl chloride; III, propyl alcohol.

For ethyl alcohol, an excess of one mole of ester shows no effect on the rate, but half a mole of ester and half of hydrogen chloride retard the action considerably. It seems that hydrogen chloride combines with ethyl alcohol more readily than with ether. The existent measurements may be fitted by assuming that the effect of the acid on the activity coefficient of the alcohol is equal to that of an equal concentration of the alcohol itself, or that $g_{31} = g_{11}$, so that the activity coefficient may be regarded as constant during the course of the reaction, but varying with the initial concentration of alcohol. Methyl alcohol behaves similarly but $g_{31} = g_{11}$ is considerably larger than for ethyl alcohol.

Summary

There is given an analytical method for the treatment of reaction rates in non-ideal solutions where the environment changes during the course of the reaction, based on approximate equations for the change of activity coefficient with concentration.

By use of Bronsted's theory of reaction mechanism, the method is applied to the oxidation of ammonia by persulfate ion in the presence of silver ion.

The principles by which the activity coefficients in non-electrolyte mixtures may be approximately evaluated are given, and illustrated by their application to the reaction of p-nitrobenzoyl chloride with certain alcohols.

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

THE PHOTOCHEMICAL DISSOCIATION OF TRIATOMIC MOLECULES. HYDROGEN CYANIDE

BY DONALD STATLER VILLARS

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The remarkable success of Franck, Kuhn and Rollefson[1] in explaining the absorption spectra of the Group I halides leads one to the query whether the same mechanism does not hold also in the case of polyatomic molecules. Its importance to photochemistry cannot be neglected, especially in view of the attempt of Franck and Scheibe[2] to explain in a reasonable manner the photolysis of hydrogen iodide in aqueous and hexane solutions. According to Franck and Kuhn[3] an "atomic"[4] molecule may be dissociated photochemically into a normal atom plus an excited atom. Only two continuous absorption regions in the near ultraviolet should result, depending on which is the one excited. On the other hand, an "ionic"[5] molecule may be dissociated photochemically into two normal atoms, one way in addition to those in which the "atomic" molecule may dissociate. In this case an extra absorption region is to be found to the red side of the spectrum and at a distance corresponding to the energy difference ${}^2P_{1/2} - {}^2P_{1\,1/2}$ of the halogen ground doublet. The first step toward the application of their theory to polyatomic molecules is the consideration of triatomic molecules. When several of these have been investigated it will be time to take up the more complicated ones. Terenin[6] has already studied triatomic molecules, two atoms of which are similar. As this is likely to lead to degeneracy complications in the analysis of the spectra, it was thought desirable to choose

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[1] Franck, Kuhn and Rollefson, Z. *Physik*, 43, 155 (1927).

[2] Franck and Scheibe, Z. *physik. Chem.*, **139A**, 22 (1928).

[3] Franck and Kuhn, Z. *Physik*, 43, 164 (1927).

[4] An atomic molecule may be defined as one which when given sufficient vibrational energy will dissociate into atoms.

[5] An ionic molecule may be defined as one which when given sufficient vibrational energy will dissociate into ions.

[6] Terenin, Z. *Physik*, 44, 713 (1927); 49, 882 (1928); Nature, 118, 843 (1926).

a triatomic molecule all three atoms of which are different. For this purpose hydrogen cyanide seemed ideal. It possesses the unique advantage (over Terenin's diatomic halides) that the spectra of its partial decomposition products are well known. Thus if hydrogen cyanide will dissociate in any of the four modes

$$\begin{aligned} HCN + E_1 &= H + C + N && (1) \\ HCN + E_2 &= H + CN && (2) \\ HCN + E_3 &= C + NH && (3) \\ HCN + E_4 &= N + CH && (4) \end{aligned}$$

we should be able to identify by its fluorescence any excited decomposition molecule which was not in a metastable state. The investigation of hydrogen cyanide seems to have an advantage over the original one of Franck and Kuhn in that we are not likely to be disappointed by getting metastable products. In this work a calculation was first made of these different dissociation energies and this was then checked by trying to locate experimentally the predicted absorption spectra of hydrogen cyanide.

The Heat of Dissociation of Normal Hydrogen Cyanide.—The heat of dissociation of normal hydrogen cyanide may be calculated from the equation

$$\begin{array}{llllll} HCN + Q & + \frac{1}{2}D_{H_2} & + \frac{1}{2}D_{N_2} & + S_C & = H + C + N \\ -1.39\text{[7]} & + \frac{1}{2}4.38\text{[8]} & + \frac{1}{2}9.5\text{[9]} & + 6.10\text{[10]} & = 11.65 \text{ v.} \end{array}$$

where Q is the heat of formation from the element molecules (values given in volts; 1 v. = 23 kilo cal.), D the heat of dissociation of the element molecules and S_C the heat of sublimation of diamond.

In order to calculate the heats of dissociation for Reactions 2, 3 and 4 we must know the heats of dissociation of the respective dissociation products. Two of these have been calculated elsewhere.[11] Heitler and Herzberg[12] have found the heat of dissociation of CN to be 9.7 v., the products being, according to Mulliken,[13] a normal ^3P C atom and an excited ^2D N atom. The dissociation of CN into two normal atoms then should be 9.7 − 2.4 = 7.3 v. The probable error in this value may amount to as much as +0.8 v. by mistaking the excitation energy of the excited atom.[14]

With these values we get for the heats of dissociation of normal hydrogen cyanide

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[7] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 591.

[8] Witmer, *Proc. Nat. Acad. Sci.*, 12, 238 (1926).

[9] Mulliken and Birge, *Nature*, 122, 842 (1928).

[10] Kohn and Guckel, *Naturwissenschaften*, 12, 139 (1924).

[11] Villars, THIS JOURNAL, 51, 2374 (1929); $D_{NH} = 4.65$ v.; $D_{CH} = 3.55$ v.

[12] Heitler and Herzberg, *Z. Physik*, 53, 52 (1929).

[13] Mulliken, *Phys. Rev.*, 32, 761 (1928).

[14] Heitler and Herzberg believe the excited atom to be a 1.6 v. ^5S C atom instead of a 2.4 v. ^2D N atom.

$E_1 = 11.65$ v. (H + C + N) $E_3 = 7.0$ (C + NH)
$E_2 = 4.35$ (H + CN) $E_4 = 8.1$ (N + CH)

These figures show that in a thermal collision process Reaction 2 should greatly outweigh the other three. The velocity of such a dissociation should be represented by an activation energy equal to or less than $4.35 \times 23 = 100$ kilo cal. A rough calculation[15] was made to see what the speed of decomposition according to (2) would be if the heat of activation were 3.1 v. At 1000°K. there should be a 0.2% change per second at 1 atm. It was a very surprising experimental observation that hydrogen cyanide gas at one atmosphere pressure did not take on any visible change when heated in a furnace at 1000°. The liquid which was condensed in the tube protruding outside the furnace, however, turned brown, showing that a slow reaction was taking place, the products probably condensing out as rapidly as they were formed.

The Photochemical Dissociation of Hydrogen Cyanide.—That hydrogen cyanide is most likely not an "ionic"[16] molecule even though it has an electric moment (it has an infra-red absorption spectrum) is attested by the fact that its ionization constant in water is 10^{-9}. If this is true, then, according to Franck's theory, a photochemical dissociation in an elementary act should not be possible unless one of the products comes off in an excited state. The excitation energies of the different products of dissociation are as follows (doubtful values given in parentheses)

$\mathrm{H} + 10.15\text{ v.} = \mathrm{H}^*$
$\mathrm{N}(2s)^2(2p)^3\ {}^4S + 2.35 = \mathrm{N}^*(2s)^2(2p)^3\ {}^2D$
$+ 10.38 = \mathrm{N}'(2s)^2(2p)^2(3s)\ {}^4P$
$\mathrm{C}(2s)^2(2p)^2\ {}^3P + (2.0)^{17} = \mathrm{C}^*(2s)^2(2p)^2\ {}^1D$
$+ (3.2)^{17} = \mathrm{C}'(2s)^2(2p)^2\ {}^1S$
NH 32: $+ 3.7 = \mathrm{NH}^*\ {}^3\Pi^{18}$
$\mathrm{CH}\ {}^2\Pi_n + 2.9 = \mathrm{CH}^*\ {}^2\Delta_i$
$+ 3.2 = \mathrm{CH}'\ {}^2\Sigma$
$\mathrm{CN}\ {}^2\Sigma + 1.8 = \mathrm{CN}^*\ {}^2\Pi$
$+ 3.2 = \mathrm{CN}'\ {}^2\Sigma$

The energies necessary for the different photochemical dissociation possibilities are then as follows

$4.35 + 1.8 = 6.2$ v. $\mathrm{H} + \mathrm{CN}^*\ {}^2\Pi$ (2a)
$+ 3.2 = 7.6$ $\mathrm{H} + \mathrm{CN}'\ {}^2\Sigma$ (2b)
$7.0 + 2.0 = 9.0$ $\mathrm{C}^*\ {}^1D + \mathrm{NH}$ (3a)
$+ 3.2 = 10.2$ $\mathrm{C}'\ {}^1D + \mathrm{NH}$ (3b)
$+ 3.7 = 10.7$ C + NH* 311 (3c)
$8.1 + 2.4 = 10.5$ $\mathrm{N}^*\ {}^2D + \mathrm{CH}$ (4a)
$+ 2.9 = 11\ 0$ $\mathrm{N} + \mathrm{CH}^*\ {}^2\Delta_i$ (4b)
$+ 3.2 = 11.3$ $\mathrm{N} + \mathrm{CH}'\ {}^2\Sigma$ (4c)

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[15] Cf. Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," Oxford, 1926, p. 91.

[16] If we may be permitted to extend the sense of Franck's definition to the case where one of the ions is diatomic.

[17] Rough estimates by Mulliken (private communication) who used Turner's method, Phys. **Rev.,** 32, 727 (1928).

[18] Cf. Mulliken, Phys. **Rev.,** 33,730 (1929).

Thus it is seen that the photochemical dissociation which takes the least amount of light energy is also that which would give a hydrogen atom and a CN molecule (this time in an excited state). Unfortunately, the only spectrograph at my disposal was an E_1 Hilger which takes photographs of wave lengths down to 2100 Å. (5.9 v.). A check over this range nevertheless seems of use to make sure we have not gone astray in the above calculations. An error of 0.8 v. in the dissociation products of CN would lower the above expected convergence limit from 6.2 to 5.4 v. (=2280 Å.), a point where we might have hopes of detecting absorption if it occurred. The presence or absence of an absorption spectrum at wave lengths below 2800 Å. (**4.35** v.) should also throw light on our conclusions as to the type of binding between the H and CN part of the molecule.

Apparatus

The hydrogen cyanide used was prepared by dropping 1-1 sulfuric acid on solid potassium cyanide.[19] The evolved gas was at first dried by passing it over a tube of phosphorus pentoxide 130 cm. long and condensed by an ice-salt (—14") mixture surrounding the first tube of a distilling train. The yield was not good and at a later date when the gas was being prepared a second time the yield was only a few per cent. This was found to be caused by the substitution of a phosphorus pentoxide drying tube **2** meters long, a close examination revealing a sirupy combination product of $P_2O_5 \cdot x$HCN. In the final apparatus no drying was attempted and the gas was purified from water by five fractional distillations. After the distillation and before sealing off, the hydrogen cyanide would be frozen in both tubes to prevent its decomposition by heat and the apparatus evacuated.[20] As it was discovered that hydrogen cyanide has marked solvent action on De Khotinsky cement, the last distillation from pyrex to the quartz absorption cell was made through a quartz–pyrex glass joint. The liquid was quite stable and did not turn brown until after its subjection to an electric discharge or to a high temperature and pressure.

By supporting the cell proper in a furnace and controlling the temperature of the ice condensed in the tube leading from the cell to a point outside the furnace, both temperature and pressure could be regulated easily. This tube dipped into a Dewar filled with a mixture of alcohol and dry ice. The temperature in the Dewar was controlled by a toluene thermometer and that in the furnace by a Chromel–Alumel thermocouple.

The furnace consisted of a specially molded porcelain core with two side tubes sticking out of its center at right angles, the smaller one to house the thermocouple leads, the larger one to introduce light for a fluorescence experiment. The core was wound with 50 feet of No. 12 Chromel wire and surrounded by a packing of Sil-o-cel. The openings were closed by fused quartz windows to prevent convection. This furnace when drawing 19 amperes from a 110-volt main would reach the temperature of 1000" in an hour and a half.

The light source used was a hydrogen discharge tube built according to the specifica-

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[19] The method recommended in "Organic Syntheses," Vol. VII, 1927, p. 50, had the great disadvantage that the sodium cyanide solution cakes and plugs up the apparatus, after which it has to be dismantled before the preparation can be continued.

[20] The hydrogen cyanide was found to gum up the mercury badly in a mercury vapor pump, so only the supporting Hi-Vac pump was used.

tions of Bay and Steiner.[21] It was found that the spectrum of such a tube cleaned itself up after several hours of running and that it was not necessary to run the discharge beforehand at a higher load in a continuous stream of hydrogen as has been recommended by other authors.

An E_1 Hilger quartz spectrograph was used. Owing to its high dispersion and the twelve quartz reflecting surfaces through which the light from the lamp had to pass, a period of thirty minutes was required to give a satisfactory exposure.

In some of the photographs the light source used was an iron arc. This was because at the crucial moment a leak had developed in the hydrogen lamp, putting it out of commission.

Results and Discussion

Absorption.—The transmission spectrum of hydrogen cyanide at 741 mm. and 25° is exactly that of the lamp for wave lengths between 2240 and 6593 Å. To investigate the region below 2240 Å., Schumann plates were used. In this case the spectrum of the iron arc is identical with that transmitted through the hydrogen cyanide (atmospheric pressure) as far as the limit of the spectrograph (2094 Å.).

In order to increase the probability of absorption at the wave lengths accessible to the quartz spectrograph, the expedient was used of raising the molecules to higher initial vibrational quantum levels by increasing the temperature of the gas. Thus, assuming the distribution law, $N = N_0 e^{-E/kT}$, at room temperature (300°K.), 2% of the molecules have an energy 0.1 v. greater than average. At 1000°K. this number has increased to 32%, while the percentage of those having 1 v. excess energy has increased from the negligible amount of 10^{-15} to 0.001%. At 1273°K. the number having 1 v. excess energy should be about 0.01%. We might, therefore, hope to increase our absorption some 10^{13} times by raising the temperature to 1000°. Of course, there are reasons why this attempt should fail. The number of absorbing molecules may still be so small as to be negligible. Moreover, in the photochemical dissociation of hydrogen chloride, absorption sets in 1.1 v, beyond the convergence limit, the distance beyond depending on the loss in stability of the molecule in the excited state. If the stability of hydrogen cyanide changed on excitation by the same amount as in hydrogen chloride, so that its absorption maximum is 1.1 v. beyond its convergence limit, then we should not be able to detect absorption until well down in the Schumann region (1700 Å.).

Our attempt was, indeed, unsuccessful. The continuous spectrum of the hydrogen discharge was photographed after passing through hydrogen cyanide at 1000" at a pressure of 1 mm. No absorption could be observed. The investigation of hydrogen cyanide in a vacuum spectrograph should prove very fruitful, but first of all the difficulties introduced by its solvent action on cements and on mercury must be overcome.

As a final resort, the hydrogen cyanide was allowed to reach atmospheric

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[21] Bay and Steiner, *Z. Physik*, 45, *337* (1927).

pressure at 1000° and the spectrum photographed from 2240 to 2800 Å. The spectrograms were run through a microphotometer but no detectable absorption was evident. Contrary to expectation, the hydrogen cyanide did not decompose rapidly under this treatment. The vapor remained perfectly colorless to the eye, but the liquid started to turn brown, and thereafter was completely changed to a brown solid within a couple of weeks. The liquid had been prepared six weeks before being used, during which time it remained perfectly clear and colorless.

The fact that hydrogen cyanide gas shows no absorption between 2800 and 2240 Å. falls in line with the assumption that it is not an "ionic" molecule. As it certainly does not show an ionic character in aqueous solution, it seems extremely doubtful that the results reported by Andant and Rousseau[22] concerning its photolysis in light of wave lengths 3650, 3130 Å. and below could have been caused by pure hydrocyanic acid.

Fluorescence.—On the chance that the sought continuous absorption might set in immediately after the calculated convergence limit, the pressure in the cell (room temperature) was reduced to about 1 mm. by freezing the hydrogen cyanide in carbon dioxide snow and the cell was illuminated with light from a silver arc, which should furnish quite a few wave lengths in the region 1967 to 1802 Å. There was no visible fluorescence (1.8 v. excitation of CN) nor ultraviolet fluorescence (3.2 v. excitation of CN). The lines appearing were the silver lines. Neither could one observe at the temperature of 1000° a visible fluorescence of the red CN bands against the background of the relatively cold window. It is not at all surprising that we have failed to excite fluorescence by the silver arc, for the intensity of its short wave lengths (1967–1802 Å.) must have been considerably reduced in the passage of the light through the air and the quartz cell wall.

Polymerization.—Either the treatment of the hydrogen cyanide gas with light of these extremely short wave lengths or else an extremely slow chemical reaction (two months) had initiated, by the time the first absorption measurements had been completed, a decomposition or a polymerization of the hydrogen cyanide liquid in the cell. This was at first indicated by a yellowish color in the liquid, which became darker and darker. I am inclined to favor the former hypothesis for the following reasons. The polymerization of hydrogen cyanide to colorless plates of $(HCN)_3$ occurs after a long period of heating of the pure substance at 100°, or after a long irradiation with sunlight in the presence of epichlorohydrin.[23] A trace of potassium cyanide or of an alkali carbonate catalyzes the polymerization of hydrogen cyanide to a black substance, out of which can be crystallized the $(HCN)_3$. Cyanogen, on the other hand, polymerizes to black or dark brown

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[22] Andant and Rousseau, Compt. *rend.*, 184, 1553 (1927).

[23] Abegg, "Handbuch der anorganischen Chemie," Leipzig, 1909, Vol. III, Part 2, p. 236.

paracyanogen. If our hypothesis is correct, it is quite reasonable that the steps should be the following

$$\mathrm{HCN} \longrightarrow \mathrm{H} + \mathrm{CN}$$
$$2\mathrm{CN} \longrightarrow (\mathrm{CN})_2 \longrightarrow (\mathrm{CN})_x$$

Further evidence that the decomposition products of hydrogen cyanide most readily obtained are H and CN is that when a faint emission spectrum was induced in the cell which contained the brown deposit, the 0,0(3), 1,1(1) and 2,2(0) CN($^2\Sigma$ − $^2\Sigma$) bands were the most intense (intensities in parentheses). Two other bands were observed, the 0,0(1) N_2^+ band and the 0,1(1) of the second positive nitrogen group. All bands were very thin and were shaded toward the violet. Still further evidence that we have here a decomposition of hydrogen cyanide rather than a direct polymerization lies in the micro-analysis of the residual gas in the cell after opening it up under water and dissolving out the hydrogen cyanide left. A small bubble of insoluble gas remained, which was introduced into the top of a tube 6.25 mm. in diameter and mixed with an approximately equal volume of oxygen gas. A platinum resistance spiral in the top of the tube was then made to glow, and after the gases were cooled, a decrease in volume of 0.053 ± 0.008 cc. had occurred. This is an indication that hydrogen was the residual gas.

Summary

Summarizing, it may be stated that our calculations of the minimum energy required to dissociate hydrogen cyanide by a photochemical act are not contradicted by any experimental results. The supposition that hydrogen cyanide is not an "ionic" molecule is supported by the fact that it has no absorption spectrum between 4.35 and 5.9 v. (2800 and 2100 Å.). The dissociation into H and CN should require the least energy thermally (4.35 v. = 100 kilo cal.) as well as photochemically (6.2 v. = 1990 Å.), compared with dissociations into CH plus N and NH plus C. Evidence has been adduced to support the hypothesis that the brown coloration which hydrogen cyanide acquires comes from an initial decomposition into H and CN and a subsequent polymerization of cyanogen to paracyanogen, rather than that it is due to a direct polymerization of the hydrogen cyanide to $(HCN)_3$.

URBANA, ILLINOIS

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

THE SOLUBILITIES OF HELIUM, NEON AND ARGON IN WATER AND SOME ORGANIC SOLVENTS

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The distribution of a solute between two solvent media has been discussed recently in two papers by Bjerrum,[1,2] in which, especially, the relationship between the partition of electrolytes and non-electrolytes is treated according to the theoretical considerations of Born.[3] While the partition coefficient V of a non-electrolyte is defined as the ratio of its equilibrium concentrations in the two media, for a binary strong electrolyte, for example, sodium chloride

$$V_{\text{NaCl}} = \sqrt{\frac{[\text{Na}^+]^{\text{II}}[\text{Cl}^-]^{\text{II}}}{[\text{Na}^+]^{\text{I}}[\text{Cl}^-]^{\text{I}}}}$$

where $[\text{Na}^+]^{\text{I}}$ denotes the concentration at equilibrium of the sodium ion in the medium I and so on.

The partition coefficient V_n of a non-electrolyte is related to A, the reversible work of transferring one molecule from its solution in one medium to a solution of the same concentration in the other medium by the formula

$$A, = kT \log, V_n$$

For the binary electrolyte sodium chloride the corresponding relation is

$$A_{\text{NaCl}} = 2kT \log_e V_{\text{NaCl}}$$

where A_{NaCl} is the reversible work of transference of an ion pair Na+ + Cl^- from the one medium to a solution of the same concentration in the other. The transference work A_{NaCl} can be split into two parts, an electrical work due to the charge on the ions and a specific work depending on the configuration of the ions. This may be expressed by the equation

$$A_{\text{NaCl}} = A_{n(\text{Na}^+)} + A_{n(\text{Cl}^-)} - E^{\text{I}}_{(\text{NaCl})} + E^{\text{II}}_{(\text{NaCl})}$$

where $A_{n(\text{Na}^+)}$ and $A_{n(\text{Cl}^-)}$ represent the transference work for molecules similar to Na^+ and Cl^- in all respects except in not being electrically charged, while $E^{\text{I}}_{(\text{NaCl})}$ and $E^{\text{II}}_{(\text{NaCl})}$ represent the electrical work of discharging the ion pair Naf + Cl^- in the media I and II, respectively. As many ions may be regarded as spherical, E^{I} and E^{II} can be calculated by means of Born's Formula

$$E_{\text{NaCl}} = \frac{\epsilon^2}{2D}\left(\frac{1}{r_{\text{Na}^+}} + \frac{1}{r_{\text{Cl}^-}}\right)$$

r_{Na^+} and r_{Cl^-} are the radii of the ions, $- \pm \epsilon$ their charges and D is the dielectric constant of the medium. The other work terms, $A_{n(\text{Na}^+)}$

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[1] N. Bjerrum and E. Larsson, *Z. physik. Chem.*, **127,358** (1927).

[2] **N. Bjerrum,** *Trans. Faraday Soc.*, **23,** 77 (1927).

[3] M. Bom, Z. ***Physik,*** **1,** 45 (1920).

and $A_{n(Cl^-)}$, cannot be calculated, but it is reasonable to suppose that they will be equal to the corresponding transference work for molecules of the inert gas type of the same size as Na^+ and Cl^-. In order to test this hypothesis it is of importance to have data for the partition coefficients of the inert gases between various solvents. With this end in view I undertook the present measurements at the suggestion of Professor Bjerrum.

Apparatus

Owing to the considerable difference between the solubilities of helium, neon and argon, apparatus of three different sizes were used. The design was based on that of v. Antropoff,[4] with certain improvements to increase the accuracy. In particular the glass spiral, used by v. Antropoff to enable the absorption bulb to be shaken independently of the rest of the apparatus, was dispensed with and the apparatus shaken as a whole; this had the double advantage on the one hand of considerably decreasing the undesirable dead space and on the other of making the apparatus less fragile and thus easier to handle.

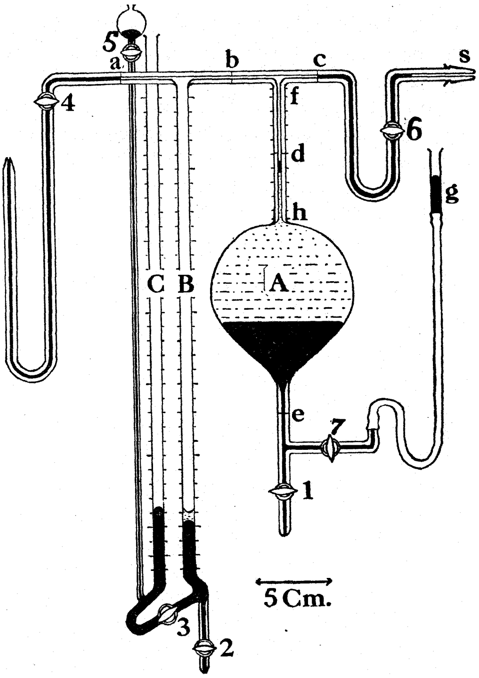

Fig. 1.

The apparatus is shown diagrammatically in Fig. 1. The absorption bulb **A** had a capacity of 88, 310 and 587 cm.^{3} in Apparatus **I, II** and **III**, respectively; the rest of the apparatus was substantially the same in all three. Behind the manometer BC, which also served as a gas buret, was a scale. The buret tube B had an internal diameter 0.5 cm., a length of 35 cm. and capacity of about 7 cm.^{3} The apparatus was fixed in a 4-mm. thick aluminum frame with bands of brass or where desired of transparent celluloid; the siphon beyond a was free from the frame.

Calibration,—The apparatus was placed in a specially constructed air thermostat, whose temperature could be varied from 2 to 45° and kept constant to within ±0.03°. After evacuation through **6**, mercury was let in through 1 until it filled the absorption bulb **A** and the capillary as far as b and c. By letting out mercury through 1 and weighing it the volume between b, c and d was determined; similarly the vertical capillary, which was graduated from f to h, was calibrated; finally, the volume of the absorption bulb from d to e was determined by the same method.

The coefficient of expansion of the glass was determined by measuring the capacity of the absorption bulb A at two different temperatures.

The gas buret was calibrated by a similar method from the marks a and b to the bottom by letting out mercury 0.2 cm.^{3} at a time through *2*.

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[4] v. Antropoff, *Z. Elektrochem.*, 25,269 (1919).

By reading through a telescope at a distance of 1 m. it was easy to attain an accuracy of 0.1 mm. or of 0.002 cm.^{3}

Technique.—Before each series of measurements the apparatus was cleaned throughout with a warm mixture of chromic and sulfuric acids. All the stopcocks except 6 were thoroughly smeared with Ramsay grease, the apparatus was evacuated through 6 and then, mercury being let in through 1, was filled completely as far as the open ends of the siphon tube, the manometer tube C and the movable reservoir g.

To the ground glass joint s was connected an L-tube the other end of which dipped into a bottle containing pure solvent, and solvent was drawn into A by letting mercury run out through 1. When A was half full of the solvent, the L-tube was disconnected from s, the stopcock 6 was quickly dried with cotton wool and greased. Half the remaining mercury was now let out through 1, while air dried over calcium chloride was sucked in through 6. The ground glass joint s was then connected through two drying towers containing sulfuric acid and bits of glass tubing to a manometer and an oil suction pump. By shaking the apparatus the mercury was set into wave-like motion; this facilitated the escape of air and vapor bubbles, which otherwise tended to collect at the mercury surface. When most of the air had been sucked away either bumping occurred or else vapor bubbles formed only at the surface; to reduce the loss of liquid by bumping, 6 was opened only at intervals. Usually the apparatus was kept evacuated overnight and after repeated shaking and suction through 6, one could show that all air had been removed by shaking for a time with 6 closed, letting mercury in through 7 so that the solvent surface was approximately at d and then opening 3, when the mercury would rush up the tube B, hitting the top with a metallic clang and then filling the rest of the tube as far as the solvent surface at d, no air bubbles being visible. If, on the other hand, an air bubble formed, the suction and test were repeated.

When the solvent was free from air and shut is as described in such a way that it nowhere was in contact with any stopcocks, the apparatus was placed in the air thermostat and brought to 20.0°, the temperature at which it was calibrated, the cock 3 being open. By opening 7 and moving the small reservoir g, the surface of the solvent could be kept in the vertical part of the capillary.

When the temperature was approximately correct, the apparatus was again taken out of the thermostat and the siphon tube sunk into a beaker filled with mercury; the gas which was stored over mercury in small glass vessels was sucked in through the siphon tube by closing 3 and opening 4 and 2. When the gas buret was nearly full, mercury was sucked from the beaker through the siphon tube to a, and 2 and 4 were then closed. Then by opening 7 and raising the reservoir g a few drops of solvent were pressed over into the gas buret in order to saturate the gas with the solvent vapor. After lowering the reservoir g until the solvent surface was at f and attaching rubber tubing to the glass joint s, a small quantity of mercury was blown over from the horizontal capillary to the surface of the solvent; the rest of the mercury was then sucked back to c, 3 was opened and by letting mercury out through 2 the mercury levels in the tubes B and C were adjusted to be approximately the same. The apparatus could now be brought to the exact temperature of the air thermostat without any fear of loss of gas through absorption. As the bulb A and vertical capillary hf constituted a very sensitive thermometer, it was easy to tell when temperature equilibrium was attained by the surface of the mercury in the capillary remaining steady. The height of the mercury and solvent surface in the buret tube as also that of the mercury in the open tube C were read through the telescope. The atmospheric pressure was read on a Fortinette Standard Barometer. From these data could be calculated W, the volume of the gas at standard temperature and pressure (S. T. P.).

Saturation of the solvent was brought about by letting out through 1 about 1 cm.3

of mercury, which was weighed, and then putting the apparatus into the air thermostat, where it was mechanically shaken as a whole with the frame. The rate of shaking was adjusted to be in resonance with the natural period of swing of the liquid. As absorption took place the mercury rose in the buret tube B, but by opening 5 at intervals more mercury could be let into C so as to keep the levels in C and B approximately equal. When the liquid had reached saturation, which generally took about one hour, the liquid levels in B and C were again read; from these one can calculate directly the pressure of the gas remaining and also its volume, since the volume from d to the surface of the liquid in A is equal to the volume of the weighed mercury let out through 1 corrected by an amount equal to any change in the volume of the small quantity of the solvent in b.

The thermostat temperature was then altered and the measurements of pressure and volume were repeated after saturation was attained.

At the end of series of measurements the cock 3 was closed, the ground glass joint s was connected to the suction pump and the mercury in the capillary around 6 was sucked out. Air was let in through 6 and the mercury in A was let out through 1. The volumes of the solvent, the mercury and the bulb at the various temperatures were calculated from the volumes at 20° and the various coefficients of expansion. When necessary a small correction to the volumes of the liquids and bulbs was applied for the variation of pressure in the apparatus; this was generally avoided by measuring at pressures very near that of the atmosphere.

The Materials Employed.—The helium, neon and argon were bought from Linde's Liquid Air Factory. According to their specification the helium contained as impurity only 0.5% by volume of neon, the neon only 1% of helium and the argon only 0.5% of nitrogen. The densities of the argon and neon were in agreement with this; the spectrum of the helium showed faint neon lines. For the technique of handling and storing these gases the reader is referred to Travers, "The Experimental Study of Gases." A Topler–Antropoff[4] pump was found to be especially convenient for this part of the work.

The water used had a specific conductivity 2×10^{-7}.

The methyl alcohol (Methanol B. A. S. F.) was distilled over magnesium strips freshly cut from a block.[5] The first third of the distillate was rejected.

The ethyl alcohol (Alcohol absolutus, Ph. dan.) was distilled twice over freshly prepared quick lime.[6]

The acetone (Kahlbaum's "zur Analyse") was used after showing the absence of water, aldehyde and acid.

The benzene was Kahlbaum's "zur Molekulargewichtsbestimmung" and had a melting point of 5.48°.

The cyclohexane, from Poulenc Frères, was shaken for a considerable time with fuming sulfuric acid, separated in a separation funnel and shaken with water until neutral. After keeping over phosphorus pentoxide for several days, it was distilled over phosphorus pentoxide; the first quarter was rejected and the remainder had a melting point of 6.0°. Cyclohexane of this purity was used for the solubility determinations of argon. Later the remainder was distilled over sodium and a fraction with a melting point of 6.3° was used; previously recorded melting points are 6.4[7] and 6.5°.[8]

Cyclohexanol "pur" from Poulenc Frères was fractionated twice in *vacuo;* the fractions used had melting points of 23.6 to 23.9°; E. Schreiner and O. E. Frivold[9] found a melting point of 23.9°.

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[5] N. Bjerrum and L. Zechmeister, *Ber.*, 56,894 (1923).

[6] Erik Larsson, "Inaugural Dissertation," Lund, 1924.

[7] N. Zelinsky, *Ber.*, 34,2802 (1901).

[8] Sabatier and Senderens, *Compt. rend.*, 132, 1255 (1901).

[9] E. Schreiner and O. E. Frivold, *Z. physik. Chem.*, 124, 1 (1926).

Results

The absorption coefficient α as defined by Bunsen is given by the formula

$$\alpha = \frac{(W \div w)P_0}{W_L \times P}$$

where W is the volume at S. T. P. of the gas originally introduced; w is the volume at S. T. P. remaining after absorption; W_L is the volume of the

TABLE I

SOLUBILITY OF HELIUM

Solvent	Complete list of measurements of a				
	15.0°	20.0°	25.0°	30.0°	37.0°
Water	0.0089	0.0089		0.0086	
	.0088	.0087		.0086	
Methyl alcohol	.0297	.0312	0.0327	.0342	
	.0298	.0314			
Ethyl alcohol	.0270	.0281		.0304	
	.0266	.0283		.0309	
Acetone	.0279	.0295	.0319		
	.0285	.0310	.0332		
	.0284	.0309	.0331		
Benzene	.0165	.0180	.0193		
		.0180	.0192	.0201	
	.0165	.0179	.0190	.0200	
Cyclohexane	.0221	.0239		.0270	
	.0220	.0232		.0265	
Cyclohexanol			.0099	.0102	0.0117
			.0102	.0112	.0121

TABLE II

SOLUBILITY OF NEON

Solvent	Complete list of measurements of a							
	5.0°	10.0°	15.0°	20.0°	25.0°	30.0°	37.0°	45.0°
Water	0.0119	0.0115		0.0103	0.0102		0.0096	0.0094
	.0117	.0111		.0103			.0096	.0094
	.0119	.0113		.0105			.0098	
Methyl alcohol			0.0413	.0432			.0478	
				.0428		0.0460		
Ethyl alcohol			.0381	.0398			.0443	
			.0380	.0407	.0417			
Acetone			.0428	.0456	.0482			
				.0470	.0498			
			.0410	.0430	.0450			
Benzene		.0233		.0269			.0333	
		.0239		.0273			.0328	
Cyclohexane			.0334	.0354		.0393		
			.0327	.0353	.0373	.0391		
Cyclohexanol					.0151	.0160	.0169	
					.0153		.0174	

solvent at the temperature of saturation; P is the partial pressure of the gas in mm. of mercury and P_0 is 760 mm.

In Tables I, II and III are collected all of the results of the measurements in the Bunsen coefficient, a. For convenience of reference from these average values at 15, 18, 20, 25, 30 and 37° have been calculated, and collected in Tables IV, V and VI, the Ostwald partition coefficients, I, which

TABLE III

SOLUBILITY OF ARGON

Complete list of measurements[a] of a

Solvent				18.0°	20.0°	25.0°	35.0°	37.0°	40.0°
Water	0.0505$^{1.65}$		0.0338$^{19.9}$	0.0349		0.0315	0.0271	0.0287$^{30.0}$	0.0254
		.0387$^{12.4}$			0.0334				.0251
Methyl	.259$^{5.1}$	.257$^{8.0}$	.254$^{13.0}$		.249	.246		.240	
alcohol	.259$^{6.0}$	.257$^{8.0}$	.254$^{14.0}$	.251	.250	.245		.242	.239$^{45.0}$
		.267$^{8.0}$	.254$^{13.0}$	.250	.250	.245		.240	
Ethyl	.248$^{1.9}$			.242	.239	.237	.232		.235
alcohol					.238				
					.243				
EtOH–H_2O		.109$^{12.5}$		.109			.110		
equivalent amounts									
Acetone	.268$^{5.0}$		.271$^{14.0}$	.272		.274	.278		.281
		.270$^{10.0}$				.274	.278		
	.269$^{6.0}$		.271$^{13.0}$	.272	.272	.274		.279	
Benzene			.220$^{13.0}$	.220	.221	.222	.224		
			.217$^{14.0}$	.217	.217	.217	.219		
			.219$^{13.0}$	.221	.222	.223	.227		
Cyclohexane			.308$^{10.0}$	.307	.306	.305		.302	
			.309$^{10.0}$	,307	.307	.305		.305	
				.306	.306	.304		.301	
Cyclohexanol						.113		.115	.117$^{45.0}$
						.112		.114	.116$^{45.0}$
						.112		.113	.114$^{45.0}$

[a] Small superior figures on measurements indicate the temperatures at which they **were** made.

TABLE IV

SOLUBILITY OF HELIUM

Solvent		15°	18°	20°	25°	30°	37°
Water	α	0.0089	0.00885	0.0088	0.0087	0.0086	0.0084
	l	.0094	.0094	.0095	.0095	.0095	.0095
Methyl alcohol	α	.0298	.0307	,0313	.0328	.0343	.0364
	l	.0314	.0327	.0336	.0358	.0381	.0413
Ethyl alcohol	α	.0268	.0275	.0281	.0294	.0306	.0325
	l	.0283	.0293	.0302	.0321	.0340	.0369
Acetone	α	.0284	.0299	.0309	.0331	...	...
	l	.0300	.0319	.0332	.0361	...	...

TABLE IV (Concluded)

Solvent		15°	18°	20°	25°	30°	37°
Benzene	α	.0165	.0174	.0180	.0192	,0202	.0221
	l	.0174	.0186	.0193	.0210	.0224	,0251
Cyclohexane	a	.0220	.0227	.0236	.0252	.0268	.0293
	l	.0232	.0242	.0253	.0275	.0297	,0333
Cyclohexanol	a	...	...	...	.0100	.0107	.0119
	l	...	...	...	.0109	.0119	.0135

TABLE V
SOLUBILITY OF NEON

Solvent		15°	18°	20°	25°	30°	37°
Water	α	0.0108	0.0105	0.0104	0.0101	0.0099	0.0096
	l	.0114	.0112	.0112	.0110	.0110	.0111
Methyl alcohol	α	.0413	.0423	.0430	.0444	.0459	.0480
	l	.0436	.0451	.0462	.0485	.0509	.0545
Ethyl alcohol	α	.0381	.0394	.0402	.0417	.0433	.0442
	l	.0402	.0420	.0431	.0455	.0481	.0502
Acetone	α	.043	.045	.046	.048		
	l	.045	.048	.049	.052	...	
Benzene	α	.0254	.0264	.0271	.0288	.0306	.0330
	l	.0268	.0281	.0291	.0314	.0340	.0375
Cyclohexane	α	.0333	.0345	.0353	.0373	.0392	.0419
	l	.0351	.0368	.0379	.0407	.0435	.0476
Cyclohexanol	α	...	...	...	.0152	.0161	.0173
	l	...	...	...	.0166	.0179	.0196

TABLE VI
SOLUBILITY OF ARGON

Solvent		15°	18°	20°	25°	30°	37°
Water	α	0.0371	0.0349	0.0336	0.0314	0.0289	0.0264
	l	.0391	.0372	.0361	.0343	.0321	.0300
Methyl alcohol	α	.253	.251	.250	.245	.243	.240
	l	.267	.267	.268	.267	.270	.273
Ethyl alcohol	α	.243	.242	.240	.237	.234	.231
	l	.256	.258	.258	.258	.260	.262
Acetone	α	.271	.272	.273	.274	.276	.279
	l	.286	.290	.293	.299	.306	.317
Benzene	α	.220	.221	.221	.222	.222	.222
	l	.232	.236	.237	.242	.246	.252
Cyclohexane	α	.308	.307	.306	.305	.304	.303
	l	.325	.327	.328	.333	.337	.344
Cyclohexanol	α	...	...	...	.112	.113	.114
	l	...	...	...	.122	.125	.129

is the equilibrium distribution ratio of the volume concentrations of the gas in the solution and in the vapor phase. The relation between 1 and *a* is $1 = \alpha T/273$, where T is the absolute temperature at which the measurement was made.

Comparison with Older Measurements.—In Tables VII, VIII and IX the results of the present measurements are compared with those of former workers. From here onward the expression solubility will always mean the Ostwald coefficient, *l*. The careful measurements of Cady, Elsey and Berger[10] of the solubility of helium in water are in good agreement with our own, but those of v. Antropoff[4] and Estreicher[11] are not. The last mentioned measurements are very uncertain for three reasons: first, the volume of gas absorbed was small in comparison with the total volume used; second, owing to the large dead space, it was often necessary to let in the gas in two portions; third, he attempted to measure the volume of gas in the dry state, which is practically impossible. V. Antropoff's measurements of the solubility of neon in water are uncertain because he used only 26 cm.^{3} of water, and of a total volume of 6.1 cm.^{3} of neon no more than 0.3 to 0.6 cm.^{3} was absorbed. The large increase of solubility with rising temperature found by v. Antropoff with neon seems improbable, when contrasted with the behavior of helium and argon.

TABLE VII

l-VALUES FOR HELIUM IN WATER

Temp., °C.	Estreicher	v. Antropoff	Cady, Elsey, Herger	Lannung
15	0.0147	0.0104	0.00933	0.0094
25	.0150	.0109	,00940	.0095
30	.0153	.0111	.00928	.0095

TABLE VIII

l-VALUES FOR NEON IN WATER

Temp., °C.	v. Antropoff	Lannung
10	0.0122	0.0117
20	.0158	.0112
30	.0175	.0110

TABLE IX

1-VALUES FOR ARGON IN WATER

Temp., °C.	Estreicher	Winkler	Lannung
10	0.0469	0.0435	0.0426
20	.0407	.0376	.0361
30	.0361	.0333	.0321

Winkler's[12] measurements of the solubility of argon in water are in fair agreement with our own, but those of Estreicher again deviate from ours. Ramsay, Collie and Travers[13] find that one volume of water at 18.2° absorbs 0.0073 volume of helium, but, as they state in the same paper that helium is insoluble in ethyl alcohol and benzene, these measurements can only have been provisional.

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[10] Cady, Elsey and Berger, THIS JOURNAL, 44,1456 (1922).

[11] T. Estreicher, *Z. physik. Chem.*, *31*, 176 (1899).

[12] L. W. Winkler, *ibid.*, 55,344 (1906).

[13] Ramsay, Collie and Travers, J. *Chem. Soc.*, *67*, 684 (1895).

Effect of Temperature on Solubilities.—As seen from the tables the solubility of each of the three gases is least in water; in the organic solvents the order of the solubilities is roughly but not exactly the same for all three gases. In each solvent helium has the smallest and argon the greatest solubility. All the solubilities are less than 0.5. In the organic solvents the solubility increases with rise of temperature and in general the more so the lower the solubility. This holds always when comparing the three gases in a given solvent and generally when comparing the various solvents for a given gas. These features can be clearly seen from Fig. 2, in which $-\log_{10} l$ is plotted against $1/T$. In this figure are included as well as our own measurements those of v. Antropoff[4] for krypton and xenon, as well as Ramstedt's[14] measurements for radon. Apart from water, whose behavior will be discussed later, in all cases straight lines are obtained and in

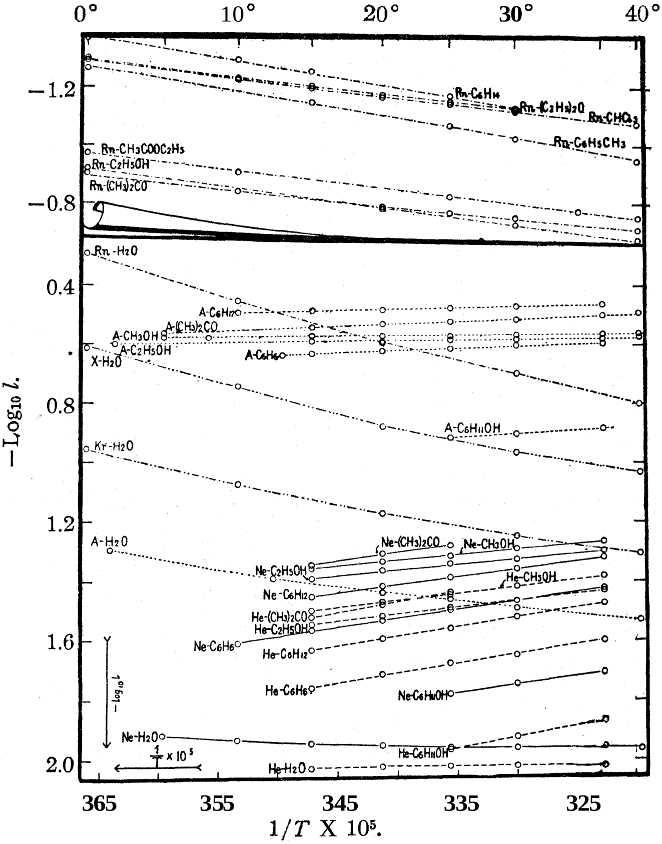

Fig. 2.—Solubility-temperature curves.

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[14] E. Ramstedt, *Le Radium*, 8, 253 (1911), figures taken from A. Schulze, *Z. physik. Chem.*, 95, 257 (1920).

general the higher the line the smaller the gradient. In the case of radon, where the solubility is especially high, being over 1, the gradients are negative; that is to say, the solubility decreases with increase of temperature and the more the greater the solubility. It appears that as the temperature increases, the solubility in all cases tends toward a number of the order of magnitude unity. An apparent exception to this regularity is the behavior of xenon in aniline; as its solubility is about 0.5, we should expect it to vary only slightly with the temperature; however, v. Antropoff himself admits these measurements to be uncertain.

This regularity also holds for the diatomic molecules H_2, N_2, CO and also for CO_2 in organic solvents with exception of H_2 in aniline.[15] Apparently the generally accepted idea that the solubility of gases decreases with rise of temperature is due to most measurements having been made with water as solvent, whereas it is clear from the figure that water behaves quite exceptionally as compared with organic solvents, for water as contrasted with the other solvents straight lines are not obtained. As water in liquid state is so highly associated at low temperatures, one would expect anomalies in the temperature coefficient of many of its properties; among these are its dissolving power of both monatomic and diatomic gases. De Villard[16] and De Forcrand[17] show the formation of a crystalline hydrate of argon at 0° and 150 atm. This shows the existence of strong attraction between water and argon molecules. Corresponding hydrates of neon and helium are not known and the temperature–solubility curves also deviate less from normal behavior, the solubility of helium in water being almost independent of the temperature. It seems not unlikely that there exist organic solvents, especially those with small polar molecules, whose behavior would be intermediate between normal and–that of water.

From the Clapeyron–Clausius equation

$$\frac{d\ \log_e l}{d(1/T)} = \frac{u}{R}$$

where u is the heat of solution at constant volume, it is clear that straight lines in Fig. 2 denote u constant over the temperature interval in question. As already mentioned this is the case for all the solvents used except water.

Integration of this equation for constant u gives

$$\log_e l = \frac{u}{RT} + \log_e a$$

or

$$l = a\ e^{u/RT}$$

The values of u and a can be obtained directly from the slopes and intercepts on the axes of the straight lines. In Table X are given the values

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[15] G. Just, *Z. physik. Chem.*, 37,342 (1901).

[16] De Villard, *Compt. rend.*, 123,377 (1896).

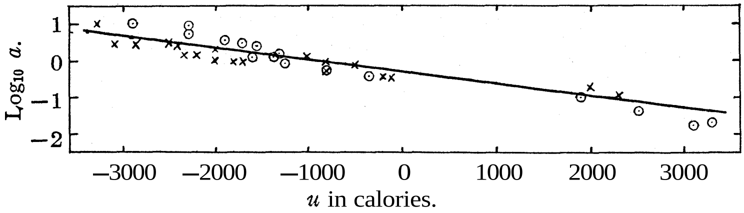
[17] De Forcrand, *ibid.*, 176, 355 (1923).

TABLE X

VALUES OF u AND LOG_{10} a

Solvent		He	Ne	A	Rn	H_2	N_2	CO	CO_2
Methyl alcohol	u	–2200	–1700	– 200		–1600	–1700	–2300	3100
	$\log_{10} a$	0.15	–0.05	–0.44		0.065	0.38	0.97	–1.77
Ethyl alcohol	u	–2000	–1800	–100	2300	–1250	– 800	– 360	2500
	$\log_{10} a$	0.0	–0.03	– 0.5	–0.95	–0.07	–0.27	–0.46	– 1.4
Acetone	u	–3300	–2000	– 800	2000	–2900	–1900	–1550	3300
	$\log_{10} a$	0.97	0.29	0.05	–0.74	1.0	0.54	0.47	– 1.7
Benzene	u	–2850	–2700	–1000		–2300	–1370	–1300	1900
	$\log_{10} a$	0.42	0.49	0.12		0.58	0.06	0.17	– 1.0
Cyclohexane	u	–2850	–2400	– 500					
	$\log_{10} a$	0.42	0.39	–0.13					
Cyclohexanol	u	–3100	–2500	– 800					
	$\log_{10} a$	0.35	0.07	– 0.30					
Molar latent heat of evap.		20	450	1500	4000	100	670	1400	3800

of u in calories and of $\log_{10}$ a obtained from our own measurements as well as those of Just and of Ramstedt. Values are also given for the heat of evaporation of the solutes in the pure state at their respective boiling points under a pressure of one atmosphere. The data for radon and neon are taken from Gmelin's "Handbuch der anorganischen Chemie," and the remainder from "International Critical Tables," Vol. 5. It is interesting to see that in going from helium to neon and from neon to argon the differences in the heats of solution are approximately the same as the differences in the heats of evaporation for the pure liquids.



×, 1-atomic; O, 2-3-atomic.

Fig. 3.

From Fig. 3, in which $\log_{10}$ a is plotted against u, it appears that there is an approximate linear relation between them. If u is measured in calories, the relation is approximately

$$-\log_{10} a = 0.3 + \frac{u}{3000}$$

It has been suggested on theoretical grounds by Tammann[18] that a should have the value unity. As already mentioned, this suggestion is not quite in agreement with our experimental results.

[18] G. Tammann, *Z. anorg. allgem. Chem.*, 158, 17 (1926).

With a view to the later application of the measured solubilities to the determination of the hypothetical partition coefficients of monatomic molecules of arbitrary size, it is of importance to study the possibility of interpolation of the partition coefficients of helium, neon and argon between the various solvents. In Table XI are given the partition coefficients V and the partition exponents $\log_{10} V$ between cyclohexane and the other solvents at 25°. Cyclohexane has been chosen as standard because it is non-polar and so not associated. The partition coefficient with benzene is nearly the same for the three gases, the solubility in benzene being 30% less. The partition coefficient with cyclohexanol, which contains a polar hydroxyl group, is about 2.5, and is greatest for argon. In the remaining cases the partition coefficient also increases in the order helium, neon and argon. The differences in the partition exponents $\log_{10} V_A - \log_{10} V_{He}$ and $\log_{10} V_A - \log_{10} V_{Ne}$ are given in Cols. 4 and 5 in Table XI. They decrease in the same order as the dielectric constant, D, but there is not exact proportionality.

Table XI

Partition Coefficient and Partition Exponent (25°)

		He	Ne	A	$\log_{10} V_A/V_{He}$	$\log_{10} V_A/V_{Ne}$	D	$\frac{D}{\log_{10} V_A/V_{He}}$	$\frac{D}{\log_{10} V_A/V_{Ne}}$
Cyclohexane	V	1.31	1.25	1.37	0.0194	0.0261	2.26	116	87
Benzene	$\log_{10} V$	0.1173	0.1106	0.1367					
Cyclohexane	V	2.52	2.45	2.73	.0348	.0470	15	430	320
Cyclohexanol	$\log_{10} V$	0.4014	0.3892	0.4362					
Cyclohexane	V	0.76	0.78	1.11	.1645	.1532	21	127	140
Acetone	$\log_{10} V$	−0.1192	−0.1079	+0.0453					
Cyclohexane	V	0.86	0.895	1.29	.1761	.1588	26	147	165
Ethyl alcohol	$\log_{10} V$	−0.0655	−0.0482	0.1106					
Cyclohexane	V	0.77	0.84	1.245	.2087	.1709	31	148	181
Methyl alcohol	$\log_{10} V$	−0.1135	−0.0757	0.0952					
Cyclohexane	V	2.90	3.70	9.8	.5288	.4230	80	154	190
Water	$\log_{10} V$	0.4624	0.5682	0.9912					

The present research was carried out at the Chemical Laboratory of the Royal Veterinary and Agricultural College, Copenhagen. I am much indebted to Professor Bjerrum for his continuous interest in my work and for providing such good facilities.

Summary

1. The solubilities l, of helium, neon and argon in water, methyl alcohol, ethyl alcohol, acetone, benzene, cyclohexane and cyclohexanol were determined in the temperature interval 15 to 37°.

2. Log l varies linearly with $1/T$ for the organic solvents, but not for water.

3. In the formula $l = ae^{u/RT}$, where u is the heat of solution, it is found that for monatomic molecules, diatomic molecules and for carbon dioxide there is an approximate linear relation between log a and u.

COPENHAGEN, DENMARK

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

STUDIES ON THE THERMOCHEMISTRY OF THE COMPOUNDS OCCURRING IN THE SYSTEM $CaO-Al_2O_3-SiO_2$. II. THE HEAT OF SOLUTION OF CALCIUM HYDROXIDE IN $HCl\cdot200H_2O$[1]

BY THORBERGUR THORVALDSON AND WELDON G. BROWN

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Introduction

Thomsen[2] reports two determinations of the heat of solution of hydrated lime in $HCl\cdot300H_2O$, giving the values 30.41 and 30.57 or a mean of 30.49 kg. calories per mole. The calcium hydroxide is described by Thomsen as a moist powder, 80.88 g. of the material containing 74 g. of $Ca(OH)_2$. Berthelot[3] determined the heat of solution of calcium hydroxide in water and the heat of neutralization of the solution by hydrochloric acid (1 equivalent in 2 liters). He obtained thus the value 30.96 kg. calories per mole for the heat of solution of calcium hydroxide in hydrochloric acid.

An accurate value for the heat of solution of calcium hydroxide in $HCl\cdot200H_2O$ was required in connection with the present studies. Since the two values given above differ by 1.5% and are for different concentrations of acid, it was decided to redetermine the heat of this reaction.

Apparatus and Experimental Procedure

The calorimeter was of the Richards adiabatic type, with a modification in the method of stirring which prevented diffusion or convection of air between the calorimeter and the environment. The stirrer, the Reckmann thermometers and the method of introducing the sample into the calorimeter are described in the first paper of this series.[4]

The air gap between the calorimeter can and the jacket was 6 mm. wide. A negative thermal head[5] of 0.01 ± 0.005° was maintained between the outside jacket and the calorimeter. It was found that fluctuations in

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[1] The authors take pleasure in acknowledging generous financial assistance from the National Research Council of Canada.

[2] Thomsen, "Thermochemische Untersuchungen," 1883, Vol. 3, p. 248.

[3] Berthelot, *Ann. chim. phys.*, [5] *4*, 531 (1875).

[4] Thorvaldson, Brown and Peaker, THIS JOURNAL, 51, 2678 (1929).

[5] Thermal head: temperature of calorimeter *minus* temperature of jacket.

the thermal head within these limits did not introduce an appreciable error since the leakage under a negative thermal head of 0.020 ± 0.001°, with a heat capacity of 598 cal./deg., was only 0.001° for thirty-minute intervals. Under a negative thermal head of 0.05° the rise in temperature per ten-minute interval was 0.002° while the corresponding value for a head of 0.10° was 0.0045°. Barry[6] has shown that wider air gaps than the one used in this work decrease the thermal leakage materially for heads of 0.05° and higher; but as the leakage for the thermal head maintained in the determinations described in this paper was negligible, the small air gap was used in preference to a wider one in order to reduce the volume of air in the calorimeter and the uncertain correction for vaporization.

Specific Heats.—The values used in calculating the heat capacity of the calorimeter system were: gold,[7] 0.031; gold alloy (80% **Au,** 20% Cu)[7] 0.044; $Ca(OH)_2$,[7] 0.27; $HCl \cdot 200H_2O$[8] (18 to 20°), 0.9826 (20° cal.). All weights were corrected to vacuum.

Purification of Materials

Calcium Carbonate and Calcium **Oxalate.**—The general procedure used in the preparation of pure calcium oxide is described in the first paper of this series. Similar precautions were taken to assure purity of reagents, thorough washing of precipitates and separation of mother liquors and wash waters. The acids and other reagents were always either freshly redistilled or freshly recrystallized when used.

Sample A.—Calcium carbonate was dissolved in hydrochloric acid, reprecipitated from dilute solution by ammonium carbonate, redissolved in hydrochloric acid and the calcium precipitated as the oxalate by ammonium oxalate.

Sample **B.—Calcium** nitrate was recrystallized eight times and the calcium precipitated as calcium carbonate. The carbonate was then dissolved in hydrochloric acid and the calcium precipitated from a hot dilute solution as the oxalate.

Sample C.—A very pure sample of calcium nitrate was recrystallized twice in vessels of fused silica and the calcium precipitated as the carbonate,

Sample D.—A very pure sample of recrystallized calcium chloride was treated with excess of bromine and milk of lime, boiled, filtered and changed to the nitrate by repeated evaporation with excess of nitric acid. The solution was filtered and the nitrate was then recrystallized five times in glass and three times in platinum vessels and the calcium precipitated as calcium carbonate (calcite).

Sample E.—Calcium nitrate of high purity was treated with excess of bromine and milk of lime, boiled, filtered, recrystallized twice and the calcium precipitated as calcium carbonate (calcite).

$HCl \cdot 200H_2O$.—The acid was first redistilled, the condenser tube being fused silica, the middle fraction collected in silica flasks and diluted to $HCl \cdot 200H_2O$. The adjustment was made by titrations with pure sodium carbonate and by gravimetric determinations of chloride.

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[6] Barry, THIS JOURNAL, *44*, 921 (1922).

[7] "International Critical Tables," 1929, Vol. V, pp. 92, 120, 99.

[8] Richards, Mair and Hall, THIS JOURNAL, 51,727 (1929). This is calculated from the values in mayers for 18 and 20° given in Table I, p. 729. According to a private communication from Dr. Mair, the values given in calories for $HCl \cdot 200H_2O$ at 18 and 20° **are** in error.

Saturated Lime-Water.—Excess of pure calcium oxide was shaken with freshly redistilled carbon dioxide-free water. The saturated solution was allowed to stand in contact with excess of calcium hydroxide and was protected from contamination with carbon dioxide.

Preparation of Calcium Hydroxide.—Calcium oxide was prepared from the pure samples of calcium carbonate and calcium oxalate as required, by ignition in platinum crucibles to constant weight in an electric muffle. The oxide was then hydrated in two different ways: by prolonged exposure to water vapor in an evacuated vessel at 21°, or by exposure to saturated steam in an autoclave at 150° for twenty-four hours or more. Precautions were taken to prevent access of carbon dioxide to the material during the preparation. The crucibles were then transferred to a vacuum desiccator over calcium oxide and kept there until constant in weight, when the heat of solution of the material in $HCl \cdot 200H_2O$ was determined. Determinations of the heat of solution of samples hydrated at 21°, containing on the average 13% of water in excess of that required to form $Ca(OH)_2$, were also made. The results are recorded in Tables I, II and III.

It was found that the calcium oxide placed over water in an evacuated vessel absorbed water vapor very rapidly until it had taken up 11 to 15% in excess of the amount required to form calcium hydroxide. All except the last few tenths of a per cent. of this excess of water was removed when the crucible was placed in vacuum over calcium oxide. This last portion of water was held very firmly and was not removed from the samples used for determining the heat of solution. The material prepared in steam at 150° differed in this respect and was almost of the theoretical composition after drying over calcium oxide. When samples of calcium hydroxide, prepared by the two methods and dried to constant weight over lime, were exposed over a saturated solution of ammonium sulfate at 21° (aqueous tension about 15 mm.) the hydroxide which had been prepared at room temperature took up from 3 to 8 times as much water during twenty-four hours of exposure as samples hydrated in steam at 150°.

Microscopic examination of the samples of calcium oxide and of the calcium hydroxide prepared from it by the two methods indicated marked physical differences. The particles of calcium oxide retained the shape and the size of the calcite crystals from which they were formed by ignition. They were weakly birefringent. Hydration by exposure of the ignited calcite to water vapor at 21° still left the shape and size of particles unchanged. The hydrated material had a refractive index[9] of 1.573 ± 0.002 and appeared very weakly birefringent when the sensitive tint plate was used.

The samples prepared by hydration of the ignited calcite in steam at 150° were composed of plates and prisms which were anisotropic and had the indices of refraction given by Ashton and Wilson.[10]

It seems probable that the particles of the calcium hydroxide prepared at 21° have a very large internal as well as external surface and that this is the reason for the large capacity of the material for taking up water vapor.

The literature contains some evidence for the formation of a dihydrate of calcium oxide below 60°. Haslam, Calingaert and Taylor[11] attempted

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[9] Measurements by V. A. Vigfusson.

[10] Ashton and Wilson, *Am. J. Sci.*, 13, 218 (1927).

[11] Haslam, Calingaert and Taylor, THIS JOURNAL, **46**, 308 (1924).

without success to prepare this hydrate and, further, found no evidence for its existence from their study of the solubility curve for calcium hydroxide. The relative values obtained for the heat of solution of calcium hydroxide as given in Tables I, II and III do not indicate the formation of a higher hydrate when calcium hydroxide takes up water vapor at 21°.

TABLE I

HEAT OF SOLUTION OF CALCIUM HYDROXIDE, PREPARED BY EXPOSURE OF CaO TO WATER VAPOR AT 21° WITH SUBSEQUENT DRYING OVER CaO, IN $HCl\cdot 200H_2O$

Sample	CaO, g.	H_2O taken up, %	H_2O excess, %	Final temp., °C.	Corr. rise, °C.	Heat of soln. per gram of CaO, cal 20°
B	2.2468	32.73	0.60	19.87	2.080	553.8
C	1.9967	32.49	.36	20.04	1.850	554.2
C	2.2470	32.50	.37	20.05	2.083	554.6
C	2.2304	32.54	.41	20.04	2.069	554.9
C	2.2506	32.44	.31	19.96	2.083	553.7
C	2.2293	32.53	.40	19.98	2.061	553.0
C	2.2257	32.34	.21	20.04	2.058	553.1
D	2.2200	32.74	.61	20.01	2.056	554.0
D	2.2099	32.72	.59	20.00	2.045	553.6
Mean		32.56	.43	20.00		553.8

TABLE II

HEAT OF SOLUTION OF CALCIUM HYDROXIDE, PREPARED BY EXPOSURE OF CaO TO SATURATED STEAM AT 150° WITH SUBSEQUENT DRYING OVER CaO, IN $HCl\cdot 200H_2O$

Sample	CaO, g.	H_2O, taken up, %	H_2O excess, %	Final temp., °C.	Corr. rise, °C.	Heat of soln. per gram of CaO, cal 20°
A	1.9055	32.19	0.06	20.03	1.754	550.7
C	2.4333	3202	− .11	20.17	2.242	551.1
C	2.2345	32.07	− .06	19 99	2.057	550.7
C	2.1603	32.08	− .05	19.97	1.989	550.5
C	2.1969	32.11	− .02	19.98	2.023	550.9
D	2.2268	32.08	− .06	20.01	2.053	551.5
D	2.2399	32.04	− .09	20.06	2.061	550.4
Mean		32.08	− .05	20.03		550.8

TABLE III

HEAT OF SOLUTION OF CALCIUM HYDROXIDE, PREPARED BY EXPOSURE OF CaO TO WATER VAPOR AT 21°, CONTAINING A LARGE EXCESS OF WATER

Sample	CaO, g.	H_2O taken up, %	H_2O excess, %	Final temp., °C.	Corr. rise, °C.	Heat of soln. per gram of CaO, cal 20°.
D	2.2179	43.30	11.17	20.09	2.043	551.0
E	2.2425	47.98	15.85	19.99	2.064	550.6
E	2.2185	44.96	12.83	19.99	2.039	549 8
E	2.2333	44.96	12.83	20.04	2 057	551.0
E	2.2314	44.80	12.67	20.04	2.053	550.4
Mean		45.20	13.07	20 03		550.6

NOTES ON TABLES I, II AND III

(a) The weight of $HCl \cdot 200H_2O$ used in each experiment was 600.4 g. The water equivalent of the apparatus was 8.2 cal./deg., and the total heat capacity 598.2 $cal._{20°}$.

(b) The figures in the column headed "corr. rise" were corrected for (1) stirring, (2) stem exposed, (3) setting of thermometer and (4) variation in the temperature of the sample of calcium hydroxide from 20° at the time of introduction into the calorimeter.

Discussion of the Experimental Results

One small correction should be applied to the values obtained in Tables I, II and III. The air in the calorimeter system, which amounted to about 600 cc., was no doubt saturated with water vapor (at the tension of $HCl \cdot 200H_2O$ at 18°) at the beginning and practically saturated at 20° at the end of each experiment. The calculated amount of heat absorbed by evaporation is 0.18 calorie per gram of CaO. Applying this correction, the isothermal heats of solution of the three samples of calcium hydroxide in $HCl \cdot 200H_2O$ at 20.0° become 554.0, 551.0 and 550.8 $cal._{20°}$ per gram of CaO, or 31.06, 30.89 and 30.88 kg. $cal._{20°}$ per mole, respectively.

Thus the value obtained for the heat of solution of the calcium oxide hydrated at room temperature is 3 calories per gram higher than that obtained with the material hydrated in steam at 150°. This difference is much in excess of the probable experimental error of the determinations. Further, the material which contained on the average 0.43% of water in excess of the theoretical amount (Table I) gives a higher heat of solution than the samples which contained within 5 parts in 13,000 of the theoretical quantity of water of hydration for $Ca(OH)_2$.

The optical examination suggests that the calcium hydroxide prepared at room temperature may not be crystalline and that the two may differ in the energy of crystal lattice. The difference in the rate of adsorption of water vapor by the samples prepared by the two different methods suggests that they may differ in surface energy. Either of these, or both combined, might be the cause of the difference in the value for the heat of solution.

Photographs of the x-ray diffraction pattern of samples of calcium hydroxide prepared by both these methods were made. In each case the same diffraction pattern was obtained and this was identical with that given by Harrington.[12] The results cannot be considered to exclude entirely the possibility of differences in lattice energy at the time of the determination of the heat of solution, as in each case some time elapsed between the preparation of the sample and the making of the x-ray photograph. The samples, however, appeared unchanged when the photographs were taken.

The fact that the particles of the calcium hydroxide prepared at room temperature retained the shape and size of the calcite crystals from which they were prepared and, therefore, probably possessed internal surface,

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[12] Harrington, *Am. J. Sci.*, [5] 13, 467 (1927).

excluded the possibility of making an estimate of the relative effective surface area of the samples. An approximate measure of the surface energy of the material can, however, be obtained by determining its heat of adsorption or its heat of wetting. From Tables I and III it appears that when calcium hydroxide of the composition CaO + 32.56% of H_2O prepared at room temperature adsorbs an additional 12.6% of water vapor, 3.2 calories per gram of CaO are given out. To obtain further evidence as to differences in surface energy, the heat of wetting of samples of calcium hydroxide prepared by each of the methods was determined.

Determinations of the Heat of Wetting of Calcium Hydroxide.—The same calorimeter was used as for the determination of the heat of solution. The sample of calcium hydroxide was introduced in the usual way after the calorimeter, containing saturated lime-water, had come to thermal equilibrium at 20°. The results are given in Tables IV, V and VI.

TABLE IV

HEAT OF WETTING OF CALCIUM HYDROXIDE, PREPARED BY EXPOSURE OF CaO TO WATER VAPOR AT 21° WITH SUBSEQUENT DRYING OVER CaO, BY SATURATED LIME-WATER

Total heat capacity, 607 cal./deg.

Expt.	CaO, g.	H_2O, %	Temp. rise, 1st sample, °C.	Temp rise, other samples, °C.	Heat of wetting, cal. per g. of CaO
1A[a]	3.87	32.66	0.030		
1B	3.85	32.69		0.025	3.9
2A	3.93	32.63	.026		
2B	3.92	32.61		.021	3.3
3A	3.88	32.64	.026		
3B	3.85	32.68		.021	3.3
3C	3.87	32.65		.020	3.1
3D	3.87	32.64		.019	3.0
4	3.88	32.70	.026		3.0[b]
5	3.81	32.60	.029		3.5[b]
		32.65			3.3

[a] Each of the groups 1A and B, 2A and B, etc., represent successive runs without changing the lime-water in the calorimeter. The temperature rise for the first run of each group given in the fourth column is, in each case, a few thousandths of a degree higher than for the remaining runs in the group. This was shown, both by titration with acid and by measurement of electrical conductivity of the lime-water in the calorimeter before and after an experiment, to be due to supersaturation. The conductivity electrodes were mounted within the calorimeter and in this way it was found that the supersaturation reached a maximum in less than one minute after the first sample of calcium hydroxide was introduced and that it did not change with the addition of further samples

[b] In Experiments 4 and 5 the supersaturation was found to be 12.7 and 12.1%, respectively. A correction was made for this supersaturation, using 50 cal. per gram of CaO as the heat of solution of calcium hydroxide in water, in calculating the heat of wetting.

The occurrence of supersaturation under these conditions is of special interest since Goldammer[13] has reported that although calcium oxide is capable of forming supersaturated solutions, calcium hydroxide is not.

TABLE V

HEAT OF WETTING OF CALCIUM HYDROXIDE, PREPARED BY EXPOSURE OR CAO IN STEAM AT 150° WITH SUBSEQUENT DRYING OVER CAO IN SATURATED LIME-WATER

Expt.	CaO, g.	H_2O, %	Heat cap.. cal./deg.	Temp. rise, °C.	Heat of wetting, cal. per gram of CaO
1A	3.85	32.10	607	0.007	1.1
1B	3.85	32.08	607	.007	1.1
2A	2.2	32.11	607	.003	0.8
2B	2.2	32.17	607	.003	0.8
3A	3.96	32.15	507	.007	0.9
3B	3.95	32.19	507	.009	1.2
	Mean	32.13			1.0

No supersaturation was produced with the material hydrated in steam at 150°.

TABLE VI

HEAT OF WETTING OF CALCIUM HYDROXIDE, PREPARED BY EXPOSURE OF CAO TO WATER VAPOR AT 21° AND CONTAINING A LARGE EXCESS OF H_2O IN SATURATED LIME-WATER

Total heat capacity, 607 cal./deg.

Expt.	CaO, g.	H_2O, %	Temp. rise, °C.	Supersaturation		Heat of wetting, cal. per g. of CaO
				%	Temp. rise, °C.	
1B[a]	3.94	43.3	0.003			0.5
1C	3.95	43.7	.002			.3
2A	3.98	42.0	.007	7.8	0.005	.3
2B	4.08	42.4	.004			.6
3A	3.70	47.1	.009	8.0	.005	.7
3B	4.01	48.1	.004			.6
	Mean	44.4				0.5

[a] Each of the experiments in the same group (A, B, etc.), represents successive runs without changing the lime-water in the calorimeter. The temperature rise for the initial "A" runs is in each case a few thousandths of a degree higher than for the remaining runs (B, C) on account of supersaturation. The supersaturation as determined by titration is given in the fifth column and the rise in temperature, calculated for the supersaturation found, is given in the sixth column.

The values obtained for the heat of wetting of the various samples of calcium hydroxide indicate that difference in surface energy is at least mainly responsible for the variation in the values obtained for the heat of solution. If we subtract in each case the value obtained for the heat of wetting from the value for the heat of solution of calcium hydroxide prepared by the same method, we obtain the following results.

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[13] Goldammer, *Pharm. Centr.*, 26, 442 (1890).

Prepared by hydration	Cal. per g. of CaO
In steam at 150°	550.0
In water vapor at 21° (13% excess of water)	550.3
In water vapor at 21° (0.43% excess of water)	550.7

These values are in good agreement. While subtracting the heat of wetting does not necessarily eliminate entirely the factor of surface energy, as the material having the larger specific surface has still greater surface energy at the solid--liquid interface, yet this difference is probably small as compared with the heat of wetting. One would, therefore, expect that 550.0 $cal._{20°}$ per gram of CaO is close to the true value for the isothermal heat of solution of calcium hydroxide, possessing a negligible quantity of surface energy, in $HCl \cdot 200H_2O$ at 20°; but considering that the three values obtained above agree very nearly within the probable experimental error, it would probably be best to take the mean value 550.3 $cal._{20°}$ per gram of CaO, which corresponds to 30.85 kg. $cal._{20°}$ (129.0 Kj.) per mole of $Ca(OH)_2$.

Summary and Conclusions

1.. Calcium hydroxide prepared by three methods gave the following values for the isothermal heat of solution at 20° in $HCl \cdot 200H_2O$: (a) prepared from CaO in water vapor at 21°, dried over quicklime, 554.0 $cal._{20°}$ per gram of CaO (31.06 kg. $cal._{20°}$ per mole); (b) prepared from CaO in steam at 150°, dried over quicklime, 551.0 $cal._{20°}$ per gram of CaO (30.89 kg. $cal._{20°}$ per mole); (c) prepared as (a) but not dried over quicklime, 550.8 $cal._{20°}$ per gram of CaO (30.88 kg. $cal._{20°}$ per mole).

2. Samples of calcium hydroxide prepared by methods (a) and (b), while appearing very dissimilar under the microscope, gave the same x-ray diffraction pattern.

3. Samples of calcium hydroxide prepared by methods (a) and (c) gave supersaturated solutions when added to saturated lime-water, but samples prepared by method (b) did not behave in this manner.

4. The above three samples had the following average heats of wetting in saturated lime water at 20°: (a) 3.3, (b) 1.0, (c) 0.5 cal. per gram of CaO.

5. Subtracting the heat of wetting in each case from the corresponding heat of solution, one obtains the following values: (a) 550.7, (b) 550.0, (c) 550.3 $cal._{20°}$ per gram. The average value 550.3 $cal._{20°}$ per gram of CaO or 30.85 kg. $cal._{20°}$ (129.0 Kj.) per mole is considered to be the most reliable value for the isothermal heat of solution of calcium hydroxide in $HCl \cdot 200H_2O$ at 20°.

6. No evidence was found that a hydrate of lime higher than $CaO \cdot H_2O$ forms at 21°.

SASKATCHEWAN, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD COLLEGE]

RELATIVE RATES OF REDUCTION OF AROMATIC NITRO COMPOUNDS[1]

BY JOHN R. SAMPEY

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The method recently developed[2] for a study of the valence forces influencing the carbon–halogen bond in halogen phenols and halogen naphthols has been applied, in a slightly modified form, to the determination of the relative rates of reduction of a number of aromatic nitro compounds. The work was undertaken to obtain quantitative data upon the effect of various groups upon the rate of reduction of the nitro group to the amino group by an acid stannous chloride solution. The work was extended to show that, in addition to the nature and position of the various groups introduced into the benzene nucleus, the speed of the reduction is influenced markedly by factors which control the hydrogen-ion concentration of the solution.

Method of Reduction.—The method of reduction was briefly as follows: exactly 50.00 cc. of an alcoholic hydrochloric acid solution was pipetted into a 300-cc. Erlenmeyer flask, the air was displaced by a stream of nitrogen, just enough weighed $SnCl_2 \cdot 2H_2O$ was introduced to make the solution equivalent to exactly 50.00 cc. of a tenth normal iodine solution, the flask was placed in a thermostat heated to 75°, and when the contents of the flask had reached this temperature, a weighed sample of the nitro compound was introduced. At the end of a definite period of time the flask was removed, cooled and the excess stannous chloride titrated with a standard tenth normal iodine solution.

The addition of a weighed sample of the solid $SnCl_2 \cdot 2H_2O$ for each reduction is more tedious than the former method of using a standard solution of this reducing agent, but this method has an advantage in that it permits of a more exact control of the concentration of the reducing agent; in the former procedure some oxidation inevitably took place during the preparation of the standard solution and we were never able to prepare two solutions of exactly the same reducing strength. The weight of the $SnCl_2 \cdot 2H_2O$ required to reduce 50.00 cc. of the $N/10$ iodine solution had to be determined by actual titration, for it was found that different samples of the salt of C. P. grade varied slightly in composition. The weight used in each of the reductions reported in this paper was 0.6000 g.

The alcoholic hydrochloric acid solution used in Table I was prepared by making up 20.00 cc. of 37% hydrochloric acid to exactly one liter with 95% alcohol. This concentration of acid was more than enough to form

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[1] Presented in substance before the Organic Division of the American Chemical Society at the Detroit Meeting, September, 1927.

[2] Sampey, THIS JOURNAL, 49, 2849 (1927).

both the stannic chloride salt and the hydrochloride of the amine. The concentration of the nitro compound taken for each reduction was exactly equivalent to the concentration of the stannous chloride solution, *e. g.*, 0.0700 g. of dinitrobenzene would oxidize as much stannous chloride as 0.1025 g. of nitrobenzene. Each of the nitro compounds was carefully purified before reduction.

TABLE I

RELATIVE RATES OF REDUCTION OF AROMATIC NITRO COMPOUNDS

Compound	Wt., g.	Time, min	0.1 *N* I_2, cc.	Amt. red., %	Wt., g	Time, min.	0.1 *N* I_2, cc.	Amt. red., %
Nitrobenzene	0.1025	15	34.7	30.6	0.1025	15	34.9	30.2
o-Nitrochlorobenzene	.1313	15	11.0	78.0	.1313	15	11.0	78.0
m-Nitrochlorobenzene	.1313	15	15.3	69.4	.1313	15	15.4	69.2
p-Nitrochlorobenzene	.1313	15	22.5	55.0	.1313	15	22.3	55.4
o-Nitrobromobenzene	.1683	15	11.5	77.0	.1683	15	11.4	77.2
m-Nitrobromobenzene	.1683	15	15.1	69.8	.1683	15	14.9	70.2
p-Nitrobromobenzene	.1683	15	20.9	58.2	.1683	15	21.0	58.0
o-Nitro-iodobenzene	.2075	15	11.6	76.8	.2075	15	11.8	76.4
m-Nitro-iodobenzene	.2075	15	14.6	70.8	.2075	15	14.5	71.0
p-Nitro-iodobenzene[a]	.2075	15	20.6	58.8	.2075	15	20.7	58.6
o-Nitrotoluene	.1141	15	31.0	38.0	.1141	15	31.1	37.8
m-Nitrotoluene	.1141	15	36.3	27.4	.1141	15	36.5	27.0
p-Nitrotoluene	.1141	15	39.8	20.4	.1141	15	39.6	20.8
m-Nitraniline	.1150	10	18.0	64.0	.1150	10	18.2	63.6
p-Nitraniline	.1150	15	35.5	29.0	.1150	15	35.2	29.6
o-Nitrophenol	.1158	15	32.2	35.6	.1158	15	32.3	35.4
m-Nitrophenol	.1158	15	37.7	24.6	.1158	15	37.4	25.2
p-Nitrophenol	.1158	15	45.5	9.0	.1158	15	45.7	8.6
o-Nitrobenzoic acid	.1390	15	25.5	49.0	.1390	15	25.4	49.2
m-Nitrobenzoic acid	.1390	15	23.5	53.0	.1390	15	23.6	52.8
p-Nitrobenzoic acid[a]	.1390	15	17.5	65.0	.1390	15	17.3	65.4
m-Dinitrobenzene	.0700	10	16.6	66.8	.0700	10	16.8	66.4
p-Dinitrobenzene	.0700	10	26.2	47.6	.0700	10	26.3	47.4
2,4-Dinitrochlorobenzene	.0844	10	20.7	58.6	.0844	10	20.6	58.8
2,4-Dinitrobromobenzene	.1028	10	16.7	66.6	.1028	10	16.9	66.2
2,4-Dinitrotoluene	.0759	10	15.7	68.6	.0759	10	16.0	68.0
2,4,6-Trinitrotoluene	.0630	8	18.0	64.0	.0630	8	17.8	64.4
2,4,6-Trinitrobenzoic acid	.0715	8	19.3	61.4	.0715	8	19.6	60.8

[a] Because of the insolubility of the nitro compound, it was added before the stannous chloride; the reduction was timed from the addition of the stannous chloride, after the solution reached the temperature of the thermostat.

One of the interesting observations to be made from Table I is found in the relative rates of reduction of the ortho, meta and para isomers of the same compounds: the meta isomer lies intermediate, instead of in contrast to the ortho and para; the ortho is reduced the most rapidly, the para most slowly in every case except with the three nitrobenzoic acids. It is also worth noting that the corresponding chloro-, bromo- and iodo-nitrobenzenes are reduced at nearly the same rate; this is in sharp contrast to the effects produced on the speed of reduction by the introduction of certain of the other groups. Table I is not as complete as desired, because a number of the nitro compounds prepared and purified were too colored after reduction to permit the detection of the end-point in the iodine titration.

From the previous work[3] on the removal of halogens by acids when ortho or para to amino groups, there was the possibility that the rate reported for the reduction of o- and *p*-nitro-iodobenzene and of 2,4-dibromonitrobenzene might also be due to the removal of the positive halogen. When samples of these halogen nitro compounds were heated for more than an hour in the presence of more than enough stannous chloride to reduce all the nitro groups, there was no removal of the halogen atoms. Only when the acidity of the solution was increased several fold did we note the removal of the halogen along with the reduction of the nitro group.

Effect of Hydrogen-Ion Concentration.—An increase in the hydrogen-ion concentration of the solution had a marked effect upon the rate of reduction of the nitro compounds. The alcoholic hydrochloric acid solutions used in Table II were prepared as follows:

Solution A	37% HCl, 10.00 cc.	Water, 100.00 cc.	Abs. alcohol to 500.00 cc.
Solution B	37% HCl, 30.00 cc.	Water, 100.00 cc.	Abs. alcohol to 500.00 cc.
Solution C	37% HCl, 50.00 cc.	Water, 100.00 cc.	Abs. alcohol to 500.00 cc.
Solution D	37% HCl, 100.00 cc.	Water, 100.00 cc.	Abs. alcohol to 500.00 cc.

The accuracy with which these solutions were made may be judged by the two check analyses, for a fresh solution was prepared for each reduction. The 100.00 cc. of water included in each of these solutions was added for reasons set forth in Table III. Exactly 50.00 cc. of each of these solutions was introduced into the Erlenmeyer flask for the reduction; the quantities of the o-nitrotoluene and stannous chloride were the same as in Table I.

TABLE II

EFFECT OF ACIDITY UPON THE RATE OF REDUCTION OF O-NITROTOLUENE

	Soln. A		Soln. B		Soln. C		Soln. D	
Reduction time, min.	15	15	15	15	15	15	15	15
0.1 N iodine, cc.	37.5	37.4	32.5	32.7	28.8	28.9	18.1	17.9
Amt. reduced, %	25.0	25.2	35.0	34.6	42.4	42.2	63.8	64.2

The pronounced increase in the rate of reduction with an increase in the acidity of the solution becomes more interesting when compared with the results of Adams, Cohen and Rees[4] on the reduction of aromatic nitro compounds to amines with hydrogen and platinum-oxide platinum black as a catalyst; they found that appreciable quantities of hydrochloric acid lowered the rate of reduction.

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[3] Nicolet and Sampey, THIS JOURNAL, 49, 1796 (1927).

[4] Adams, Cohen and Rees, *ibid.*, 49, 1093 (1927).

Inhibitory Effect of Water.—In the runs reported in Table II, 100.00 cc. of water was added to each alcoholic solution in order to lessen any effects which might have been produced by a change in the moisture content as the acidity of the solution was increased. In Table III evidence is presented of just how pronounced is the inhibitory effect of water on the rate of reduction. The solutions used in Table III were made up as follows:

Solution A	37% HCl, 10.00 cc.	....,	Abs. alcohol to 500.00 cc.
Solution B	37% HCl, 10.00 cc.	Water, 30.00 cc.	Abs. alcohol to 500.00 cc.
Solution C	37% HCl, 10.00 cc.	Water, 100.00 cc.	Abs. alcohol to 500.00 cc.
Solution D	37% HCl, 10.00 cc.	Water, 190.00 cc.	Abs. alcohol to 500.00 cc.

No effort was made to prepare a more anhydrous solution than Solution A, because of the insoluble nature of $SnCl_2 \cdot 2H_2O$ in such a solution. The concentrations of o-nitrotoluene and stannous chloride were the same as in the previous reductions.

TABLE III

EFFECT OF MOISTURE UPON THE RATE OF REDUCTION OF O-NITROTOLUENE

	Soln. A		Soln. B		Soln. C		Soln. D	
Reduction time, min.	15	15	15	15	15	15	15	15
0.1 N iodine, cc.	29.5	29.6	31.3	31.0	37.5	37.4	40.8	41.0
Amt. reduced, %	41.0	40.8	37.4	38.0	25.0	25.2	18.4	18.0

Effect of Stannous Chloride Concentration.—In Table IV the concentration of the stannous chloride was varied over a wide range. If we assume from the equation

$$\underset{a}{3SnCl_2} + \underset{b}{RNO_2} + 7HCl = 3SnCl_4 + RNH_2 \cdot HCl + 2H_2O$$

that each molecule of RNO_2 which is reduced is done so rapidly and completely, then at the time t when we measure $a-x$, we must consider that the concentration of the nitro compound, b, has become $b-x/3$; *i. e.*, three moles of stannous chloride have been used for each mole of RNO_2 disappearing. Then from the integration of the equation

$$\frac{dx}{dt} = K(a - x)\left(b - \frac{x}{3}\right)$$

we obtain

$$K = \frac{-3}{t(3b - a)} \ln \frac{a(3b - x)}{3b(a - x)}$$

This equation can be used except where $a = 3b$; in Run III below, where $a = 3b$, the integration of the equation

$$\frac{dx}{dt} = \frac{K}{3}(a - x)^2$$

becomes

$$K = \frac{3x}{at(a - x)}$$

In Table IV are set forth the results of substituting the data in the above equations when the concentration of the stannous chloride was increased ten-fold. In order to reduce the effects of any change in hydrogen-ion concentration, acetic acid was used as the solvent: 50.00 cc. of water and 10.00 cc. of **37%** hydrochloric acid were added to 500.00 cc. of glacial acetic acid; 50.00 cc. of this solution and 0.1313 g. (0.0167 moles) of ***m*-**nitrochlorobenzene were introduced into an Erlenmeyer flask for each reduction. The amounts of stannous chloride ranged from 0.1500 g. to 1.5000 g., which gave a concentration in terms of moles, estimated from titrations against a standard iodine solution, of 0.0125 to 0.1250.

TABLE IV

EFFECT OF STANNOUS CHLORIDE CONCENTRATION ON THE REDUCTION OF 112-NITROCHLOROBENZENE

Run	t, min.	a	x	$a - x$	$3b - x$	K
I	15	0.0125	0.0072	0.0053	0.0428	− 3.75
II	15	.0250	.0133	.0117	.0368	3.59
III	15	.0500	.0247	.0253	.0253	3.90
IV	15.	.0625	.0286	.0339	.0215	3.76
V	15	.0750	.0315	.0435	.0186	3.59
VI	15	.1125	.0384	.0741	.0117	3.31
VII	15	.1250	.0401	.0849	.0100	3.28

Summary

1. **A** table is given of the relative rates of reduction to amines of twenty-eight aromatic nitro compounds by an acid stannous chloride solution.
2. An increase in the hydrogen-ion concentration of the stannous chloride solution increases the speed of the reduction.
3. Water has an inhibitory effect upon the speed of the reduction.
4. When the stannous chloride concentration is varied ten-fold, constants calculated for a second order reaction hold well for such a complex system.

BIRMINGHAM, ALABAMA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD COLLEGE]

THE POLARITY OF THE CARBON–HALOGEN BOND. III. THE INHIBITORY EFFECT OF WATER ON THE ACID HYDROLYSIS OF HALOGEN NAPHTHOLS[1]

BY JOHN R. SAMPEY

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The inhibitory effect of water upon reactions catalyzed by hydrogen ions has been studied intensively, although the number of different types of reactions investigated has been limited. The theories postulated to explain the phenomenon are almost as numerous as the number of investigators working in the field. A comprehensive review of the literature has appeared recently.[2] In the present investigation data are presented to show the inhibitory effect of water on another type of reaction catalyzed by hydrogen ions.

1-Iodo-2-hydroxynaphthalene was the compound selected for the determination of the effect of moisture on the rate of removal of the iodine by hydrogen ions. The method of hydrolysis was the same as that developed for the study of the relative rates of reduction of aromatic nitro compounds.[3] The alcoholic hydrochloric acid solutions used in Table I were prepared as follows.

Solution A	37% HCl, 10.00 cc.	....	Abs. alc. to 500.00 cc.
Solution B	37% HCl, 10.00 cc.	Water, 50.00 cc.	Abs. alc. to 500.00 cc.
Solution C	37% HCl, 10.00 cc.	Water, 190.00 cc.	Abs. alc. to 500.00 cc.

The insoluble nature of $SnCl_2 \cdot 2H_2O$ in absolute alcohol did not permit us to make a more anhydrous solution than Solution A; 0.3375 g. of the iodonaphthol and 0.3000 g. of $SnCl_2 \cdot 2H_2O$ (equivalent to 25.00 cc. of $N/10$ iodine solution) were added to each 50.00-cc. portion of the above solutions in the hydrolyses. The constants reported in Table I were obtained when the data were substituted in the equation for a first order reaction.[4]

TABLE I

EFFECT OF WATER ON THE HYDROLYSIS OF 1-IODO-2-HYDROXYNAPHTHALENE IN ALCOHOLIC HYDROCHLORIC ACID SOLUTION

	Soln. A		Soln. B		Soln C	
0.1 N iodine used in titrn., cc.	15.2	15.0	20.3	20.5	21.7	21.7
$k \times 10^{-2}$	3.32	3.40	1.38	1.32	0.94	0.94

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[1] The author is indebted to Dr. A. W. Homberger of the University of Louisville, in whose laboratory the major portion of this research was completed during the summer of 1928.

[2] Bronsted, Chemical Reviews, 5, 231 (1928).

[3] Sampey, THIS JOURNAL, 52, 88 (1930).

[4] Sampey, *ibid.*, 49, 2853 (1927).

When acetic acid was used as the solvent in place of the alcohol the inhibitory effect of water was even more pronounced. The acetic acid solutions were made as follows

Solution A	37% HCl, 5.00 cc.	. . . .	Gl. HAc, to 500.00 cc.
Solution B	37% HCl, 5.00 cc.	Water, 10.00 cc.	Gl. HAc, to 500.00 cc.
Solution C	37% HCl, 5.00 cc.	Water, 30.00 cc.	Gl. HAc, to 500.00 cc.
Solution D	37% HCl, 5.00 cc.	Water, 50.00 cc.	Gl. HAc, to 500.00 cc.
Solution E	37% HCl, 5.00 cc.	Water, 100.00 cc.	Gl. HAc, to 500.00 cc.

The same weights of iodonaphthol and stannous chloride were used as in the previous hydrolyses.

TABLE II

EFFECT OF WATER ON THE HYDROLYSIS OF 1-IODO-2-HYDROXYNAPHTHALENE IN ACETIC ACID SOLUTION

	Soln. A		Soln. B		Soln. C		Soln. D		Soln. E	
Time, minutes	5	5	5	5	5	5	10	10	10	10
$0.1\ N\ I_2$, cc.	11.0	11.1	8.0	8.3	12.4	12.4	11.1	11.2	20.3	20.0
$k \times 10^{-1}$	1.64	1.62	2.27	2.20	1.40	1.40	0.81	0.80	0.20	0.22

It will be noted that in Solution B the rate of removal of the iodine is faster than in Solution A, although the former contains more water. This may be explained by the observation that at the end of the five-minute period Solution A was strongly colored by iodine; this color disappeared *immediately* upon the addition of ten cubic centimeters of water. Presumably the iodine was removed more rapidly in Solution A than in Solution B, but because of the nearly anhydrous conditions existing in the former, the stannous chloride was unable to react with the liberated iodine, with the result that part of the iodine resubstituted in the naphthol. When iodine and stannous chloride were dissolved in glacial acetic acid containing a small amount of hydrochloric acid, the iodine color did not disappear until more water was added. This phenomenon made it impossible to determine the effect of small amounts of water on the rate of removal of the iodine from the iodonaphthol.

Neutral Salt Effect.—The effects of neutral salts on the reactions catalyzed by hydrogen ions have received considerable attention. In Table III some observations are recorded of the action of several inorganic salts upon the rate of hydrolysis of the positive halogen in 1-iodo-2-hydroxynaphthalene. The alcoholic solution used had to contain a large proportion of water in order to dissolve the salts, and also a large amount of hydrochloric acid to bring about the removal of the halogen from the aqueous solution; after a considerable number of solubility determinations, the solution that was used was prepared by making up 100.00 cc. of **37%** hydrochloric acid and 475.00 cc. of water to exactly one liter with 95% alcohol. The amounts of iodonaphthol and stannous chloride were the same as in the previous tables. Sufficient quantities of the dry salts were added to give a half molar concentration.

TABLE III

EFFECT OF NEUTRAL SALTS ON THE HYDROLYSIS OF 1-IODO-2-HYDROXYNAPHTHALENE

Salt	Time, min.	0.1 N I_2, cc.	$k \times 10^{-2}$	Time, min.	0.1 N I_2, cc.	$k \times 10^{-2}$
...	15	12.7	4.51	15	12.7	4.51
KCl	15	11.3	5.29	15	11.2	5.35
NaCl	15	10.8	5.59	15	10.8	5.59
KBr	15	10.5	5.78	15	10.6	5.72
NaBr	15	10.1	6.04	15	10.2	5.98
LiCl	15	10.0	6.10	15	10.2	5.98
$SnCl_4$	15	10.4	5.84	15	10.2	5.98

Stannic chloride is not a neutral salt but it was added to the list because in the former method of preparing standard solutions of stannous chloride[3] there were always appreciable quantities of this salt present due to the oxidation of the stannous chloride during storage. We were not able to include sodium or potassium iodide in Table III, because they decomposed quite rapidly with the liberation of free iodine.

Summary

1. Water decreases the rate of hydrolysis of 1-iodo-2-hydroxynaphthalene in alcoholic and acetic acid solutions of hydrochloric acid.
2. Stannous chloride and iodine do not react appreciably in hydrochloric acid solutions of acetic acid containing little moisture.
3. Neutral salts increase the rate of hydrolysis of positive halogens.

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[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY AND COLUMBIA UNIVERSITY]

THE TEMPERATURE COEFFICIENT OF REACTIONS IN SOLUTION

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The generally accepted explanation for the temperature coefficient of reactions in general is essentially the Arrhenius hypothesis of activated molecules. This has been worked out rather completely for gaseous reactions on the assumption that there is a whole series of such active molecules in statistical equilibrium with the inactive molecules and that the active molecules differ from the inactive molecules only in their energy content; each of these active molecules has a finite probability of reacting which depends upon this energy content. On this hypothesis the energy of activation is the difference of the mean energy of the molecules which react and the mean energy of all the molecules.[1] It is generally supposed that the temperature coefficients of reactions occurring in solution has a similar explanation but so far there has been no theory generally

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[1] Tolman, THIS JOURNAL, **47**, 2652 (1925).

accepted which accounts for the experimental facts observed in the study of the temperature coefficient of reactions in solution.[2] It is the purpose of this paper to discuss an application of the temperature coefficient of gaseous reactions to reactions in solution.

Bronsted's Theory.—Bronsted[3] has obtained formulas accounting for many of the apparently anomalous facts in the field of reaction kinetics involving ions. It may be assumed that the first reaction between two molecules in a solution is to form a fugitive reactive complex which is in statistical equilibrium with the reacting molecules and it is this reactive complex which decomposes spontaneously and unimolecularly or reacts with another molecule in the system. The equations representing the change may be given as

$$A + B \leftrightarrows A{\cdot}B$$
$$A{\cdot}B = C + D + \ldots.$$

or

$$A{\cdot}B + C = D + E + \ldots.$$

The velocity of the reaction is assumed to be proportional to the concentration of the fugitive reactive complex A·B. The concentration of this complex is related to its activity by the equation

$$C_{A\cdot B} = \frac{C_A C_B f_A f_B}{f_{A\cdot B}}$$

where the f's are the activity coefficients.

The success of this theory lies in its ability to predict the changes in the velocity of such reactions due to the addition of electrolytes to the solution. These additions of salts will change the activity of the ions present in accordance with the principles first proposed by Lewis and by Brönsted.[4] The theory predicts the general nature of the change in velocity due to the addition of such salts; in some cases it gives correctly the sign and magnitude of the change, which is a remarkable contribution to our knowledge of these reactions when we consider the confusion in this field before the theory was developed.

An extension of the theory has been proposed to account for the phenomenon of acid and basic catalysis. It is only necessary to replace the fugitive complex between two reacting molecules by a fugitive complex between a molecule and the hydrogen ion or the molecule and a basic ion. The reaction rate is again assumed to be proportional to the *concentmtion* of the reactive complex and this concentration is again calcu-

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[2] Christiansen, *Z. physik. Chem.*, **113**, 35 (1924), has developed a theory for the velocity of bimolecular reactions in solution.

[3] Bronsted, *ibid.*, **102**, 169 (1922); Bjerrum, *ibid.*, (a) **108**, 82 (1924); (b) **118**, 251 (1925); see also Bronsted, *ibid.*, **115**, **337** (1925).

[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**; Bronsted, THIS JOURNAL, 42, 761 (1920).

lated in the same way. Bronsted[5] was led to this concept of acid and basic catalysis from his previous proposal of a new definition of acids and bases according to which an acid is defined as a substance that can give up a proton to another molecule, while a base is one which can accept a proton from another molecule. Acid catalysis consists then in the addition of a hydrogen ion to a molecule with the subsequent reaction to give the final products and the final liberation of the proton, and basic catalysis in the addition of a basic ion to a molecule with the subsequent reaction and removal of a proton by the basic ion. Bronsted[6] has found some interesting empirical relationships between the acid and basic strength as determined from the ordinary dissociation constants of the acids and bases involved and the velocity of the reaction.

In all of this development, however, there has been a notable lack of any suggestions to account for the observed facts in connection with the temperature coefficients of these reactions. Moreover, in spite of the enormous amount of work done in support of Bronsted's theory, this work has mostly been done at only one temperature and in consequence there are comparatively few experimental data to test any theory.

Observed Temperature Coefficients.—A comprehensive review of the experimental facts has been given by Rice and his co-workers,[7] and in addition they have made the most accurate measurements of the rate of reaction between halogens and ketones in dilute aqueous solutions. They also studied the effect of adding various amounts of electrolytes and non-electrolytes. The essential observed facts are that the temperature coefficients of all these reactions are the same; when catalyzed by strong acids, the addition of salts of strong acids or non-electrolytes does not change the temperature coefficient even when present at high concentrations, though the absolute values of the reaction rate change considerably and follow the prediction of Bronsted's theory. These same reactions have a lower temperature coefficient when catalyzed by weak acids and the temperature coefficient is diminished still more by the addition of salts of these weak acids. The available data for sulfuric acid have been collected and are shown in Table I, from which it appears that there is first a rapid decrease in the energy of activation which finally approaches a constant value.

The small amount of experimental data available show that the change in temperature coefficient by changing the conditions in the solution is in general small, so that only high precision work is useful for any theory of the effect.

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[5] Bronsted, *Chem. Reviews*, 5, 231 (1928).

[6] Bronsted, *Trans. Faraday Soc.*, 630 (1928).

[7] Rice and Kilpatrick, THIS JOURNAL, 45, 1401 (1923); Rice and Lemkin, *ibid.*, 45, 1896 (1923).

TABLE I

DATA FOR SULFURIC ACID

Acid	Salt	Q
0.1 N HCl	None	20,540
1 N H_2SO_4	None	19,070
.15 N H_2SO_4	0.05 M Na_2SO_4	18,700
.1 N H_2SO_4	.434 M Na_2SO_4	17,610
.1 N H_2SO_4	.87 M Na_2SO_4	17,010
.097 N H_2SO_4	1.69 M $(NH_4)_2SO_4$	17,150

Theoretical

The Debye–Hückel theory predicts that the activity coefficient of an ion of a strong electrolyte will approach in the limit for zero concentration[8]

$$-\ln f_i = Z_i^2 \frac{e^3}{4k}\sqrt{\frac{\pi}{k}}\frac{1}{(DT)^{3/2}}\sqrt{\sum_1^s n_i Z_i^2}$$

where Z_i is the valence of the ion, e the atomic charge, K the Boltzmann constant, D the dielectric constant and N_i the number of ions of the i^{th} kind per cc. The rate of change of the In f_i with temperature is easily shown to be of the order of $2 \times 10^{-4}\sqrt{\mu}$, where μ is the ionic strength. This formula is only a limiting law and does not apply in the range of concentrations used in the experiments discussed in this paper, but it seems improbable that the change of the activities of strong electrolytes with temperature can account for more than a small part of the observed temperature coefficients of these reactions and some other hypothesis must be developed.

It has occurred to the authors that the following mechanism provides a means of accounting for the observed facts discussed in the previous section. The reactive complex postulated by Bronsted undoubtedly consists of a whole series of molecules which differ from each other only in energy content. It is only necessary to assume that the probability of a molecule (AH+) reacting is a function of its energy content and that it increases with increasing energy content. This is the generally accepted hypothesis in gaseous reactions and leads to the conclusion that the energy of activation as determined from the measured temperature coefficient of the reaction is equal to the difference of the mean energy of the molecules that react and the mean energy of all the molecules. The reaction scheme which we propose is then

$$\begin{aligned}&A + H^+ \rightleftarrows AH^+\\&AH^+ \rightleftarrows (AH^+)'\\&(AH^+)' + B = H^+ + C + D + \dots\end{aligned}$$

where $(AH^+)'$ represents a whole series of high energy molecules of the variety (AH^+). This differs from the usual scheme used by Bronsted only in the introduction of an additional step. Its extension to other

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[8] La Mer, *Trans. Am. Electrochem. Soc.*, *51*, 530 (1927).

cases besides hydrogen-ion catalysis is obvious. It remains now to show that this scheme does agree with the experimental facts.

The addition of salts to such a reaction catalyzed by a strong acid changes the velocity of the reaction by changing the concentration of the reactive complex and this change in the concentration of the critical complex is characteristic of the charges of A, (AH^+) and $(AH^+)'$ to a first approximation and is not due to any other specific properties which they may have. It, therefore, affects the whole series of molecules of the (AH+) type regardless of their energy contents. The energy distribution of these molecules will therefore not be disturbed. There is the possibility that the addition of the salt will change the probability of reaction of a given member of this series of (AH+)' molecules. However, if this were true, it would change the velocity of the reaction and it would not be possible, therefore, to predict the general nature of the primary salt effect. We conclude, therefore, that the distribution of molecules with different energy contents and their probabilities of reaction do not change with the addition of salt and, therefore, the temperature coefficient should be independent of the concentration of salts of strong acids, which is in agreement with experimental results. Rice and Lemkin[7] showed that the temperature coefficient is unchanged even when the reaction between acetone and iodine occurs in solutions of salt concentrations up to saturation, *i.* e., at concentrations far beyond the range in which Bronsted's theory for the salt effect can be applied. The addition of non-electrolytes such as methyl acetate or acetic acid did not change the velocity of the reaction, while cane sugar increased the velocity of the reaction; in no case was the temperature coefficient changed, which on our theory means that the relative concentrations of high energy and low energy (AH^+) molecules were unchanged.

We will now consider catalysis by weak acids. We have now present two acids, one being the (H_3O^+) and the other the undissociated acid molecule; the reaction will be catalyzed by both these acids and it is possible that it may also be catalyzed by the basic anion of the weak acid. Each of these simultaneous reactions will have its own characteristic temperature coefficient and in addition there may be an effect upon the measured temperature coefficient due to side equilibria changing the relative amounts of these catalysts. Rice and Lemkin[7] investigated the catalysis of the acetone–iodine reaction by weak acids and found in all cases that the temperature coefficient was decreased. The temperature coefficient of this same reaction when catalyzed by sulfuric acid is less than when catalyzed by hydrochloric acid and the addition of sulfates lowers the temperature coefficient still further; the experimental facts have been summarized in Table I.

We shall try to give a general interpretation of this behavior by considering the catalysis by sulfuric acid in detail. In this case we must consider the two simultaneous reaction schemes

$$\begin{aligned}&A + H_3O \rightleftharpoons (A\cdot H_3O^+)\\&(A\cdot H_3O^+) \rightleftharpoons (A\cdot H_3O^+)'\\&(A\cdot H_3O^+)' \longrightarrow H_3O^+ + B + C + \ldots\end{aligned}$$

and

$$\begin{aligned}&A + HSO_4^- \rightleftharpoons (A\cdot HSO_4^-)\\&(A\cdot HSO_4^-) \rightleftharpoons (A\cdot HSO_4^-)'\\&(A\cdot HSO_4^-)' \longrightarrow HSO_4^- + B + C + \ldots\end{aligned}$$

We assume that these are the only catalysts present since basic catalysis by the SO_4^{--} ion is negligible. The observed velocity is due, therefore, to the joint catalytic effect of the (H_3O^+) and (HSO_4^-) and the observed temperature coefficient will depend upon the heats of activation of $(A\cdot H_3O^+)$ and $(A\cdot HSO_4^-)$ and their relative amounts.

The observed velocity constant of the reaction k will be

$$k = \frac{k_1c_1 + k_2c_2}{c_1 + c_2}$$

where c_1 and c_2 are the concentrations of H_3O^+ and HSO_4^-, respectively, and k_1 and k_2 are the velocity constants for the reaction catalyzed by these ions at unit concentration. Since $(c_1 + c_2)$ is the total acidity we can rewrite this in the form

$$k = k_1F + k_2(1 - F)$$

where F is the fraction of the total hydrogen present as (H_3O^+). Using the values for the concentration of hydrogen ion and hydrogen-sulfate ion secured by Sherrill and Noyes[9] and the measured values for the velocity constant of the reaction as catalyzed by strong acids which we assume gives k_1 together with the measured velocity constant catalyzed by 0.08060 N sulfuric acid, it is possible to calculate k_2. Interpolating Sherrill and Noyes' data for this concentration, we secure 0.0547 and 0.02525 for the normalities of H_3O^+ and HSO_4^-, respectively. Using these values and the observed values of k and k_1, namely, 15.55 X 10^{-4} and 17.1 X 10^{-4}, we secure 12.6 X 10^{-4} for the value of k_2. Further, by extrapolating Sherrill and Noyes' data to 0.15 N sulfuric acid, we find 0.0982 and 0.0520 for the normalities of H_3O^+ and HSO_4^-, respectively. Using these values, the observed value of k_1, and the value of k_2 calculated above, we find the value of k for this higher concentration to be 15.5 X 10^{-4}. This shows that the specific velocity constant should not change with a variation of the concentration of the sulfuric acid, in agreement with observation.

The observed temperature coefficient of the reaction is given by the equation

$$\frac{d\ln k}{dT} = \frac{1}{k}\frac{d}{dT}[k_1F + k_2(1 - F)]$$

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[9] Sherrill and Noyes, THIS JOURNAL, 48, 1870 (1926).

There are two limiting cases for this relationship. In the case of strong acids $F = 1$, $k = k_1$ and the heat of activation is that for the reaction scheme I; in the case of the reaction catalyzed by sulfuric acid in *the* presence of a high concentration of sulfate, there will be only a very low concentration of hydrogen ion, and thus $F = 0$ and $k = k_2$, so that the measured heat of activation is that of scheme II. These two heats of activation are 20,540 and 17,100 cal., respectively. Without knowing the way F changes with temperature, it is impossible to calculate the intermediate values, but we can expect that there will be a gradual transition in agreement with Table I.

Similar considerations will apply to basic catalysis and ionic reactions in general but we must emphasize the point that it does not seem possible to make any sweeping generalization as to the magnitude of the temperature coefficient, since each reaction is a special case.

Summary

1. Up to the present there has been no satisfactory explanation developed for the temperature coefficient of reactions in solution. The present paper proposes such an explanation based on Bronsted's theory and current theories for the temperature coefficient of reactions in the gaseous state.

2. It is suggested that there is a whole series of fugitive complexes of the type postulated by Bronsted which differ from each other only in energy content. The energy of activation is defined as the difference between the mean energy of the critical complexes which react and the mean energy of all the molecules.

3. When there is only a primary salt effect the temperature coefficient should be independent of the addition of salt.

4. In the case of catalysis by weak acids we may expect that there will be several simultaneous reactions, each with its own characteristic energy of activation. This has been discussed for the catalysis of the acetone–iodine reaction by sulfuric acid and the experimental results are shown to be in agreement with theory.

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PHOTOCHEMICAL DECOMPOSITION OF NITROSYL CHLORIDE

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The decomposition of nitrosyl chloride under action of light has been in the past an object of some study. Kiss[1] has shown that visible light produced decomposition, but that since the nitric oxide and chlorine formed recombined in the dark, the decomposition was incomplete, a stationary state being finally reached. The temperature coefficient of the photochemical reaction was determined by him to 1.0 over the temperature range 0–78°. Bowen and Sharp[2] have carried out a determination of the quantum yield which led them to believe that 0.5 molecule was decomposed per light energy quantum absorbed. The light was used from a carbon arc and the spectral regions 4380–5000 and 4480–5200 Å. were isolated by means of filters. These authors found also that the quantum yield was unaffected by the degree of decomposition, which was followed up to 10%. They failed to notice any action of "red" light and attributed this failure to a very weak absorption by nitrosyl chloride in this spectral region. The reaction mechanism offered in explanation of their results included a primary dissociation of a nitrosyl chloride molecule into nitric oxide and a chlorine atom, followed by some secondary reactions of the chlorine atom resulting in a partial recombination of nitric oxide and chlorine. Such a mechanism, while accounting formally for the deficiency of the quantum yield from the value two, is quite unsatisfactory on closer consideration because it fails to account for the independence of the quantum yield from the degree of decomposition, thus from the concentrations of nitric oxide and chlorine present, as observed by these authors.

The absorption spectrum of nitrosyl chloride has also received some attention. Magnanini[3] finds that it consists of weak bands in the region 5300–6200 Å. with a strong absorption setting in below 5300 Å. Dr. G. Cario[4] and the writer carried out some time ago[5] a preliminary investigation of the absorption spectrum of nitrosyl chloride. It was found to have a banded structure, bands being observed even below 4000 Å., although no definite information with respect to the existence of fine structure in these bands was obtained.

The behavior of nitrosyl chloride seemed thus to offer a striking simi-

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[1] Kiss, *Rec. trav. chim.*, 42, 665 (1923).

[2] Bowen and Sharp, J. *Chem. Soc.*, 127, 1026 (1925).

[3] Magnanini, *Z. physik. Chem.*, 4, 427 (1889).

[4] Of Gottingen; at the time an International Research Fellow in Princeton.

[5] Unpublished.

larity to the decomposition of ammonia,[6] both substances having banded spectra and showing on illumination a deficient quantum yield unaffected by the presence of the reaction products and only very slightly (NH_3) or not at all (NOCl) affected by temperature. The deficiency of the quantum yield in both reactions, although receiving some consideration, has never been satisfactorily explained and further work in this direction seemed desirable. The nitrosyl chloride decomposition was chosen here because it has been less fully investigated and offers fewer experimental difficulties.

Experimental Details

Decomposition of nitrosyl chloride was measured manometrically. The pressure changes were followed by means of a quartz spiral manometer of the Bodenstein type, used as a zero instrument and connected to a differential manometer filled with α-bromonaphthalene. With this system pressure changes of less than 0.1 mm. of mercury could be measured. As the reaction vessel a pyrex tube **35** X 120 mm. with sealed-on polished pyrex plates was used. Nitrosyl chloride was prepared from nitrosylsulfonic acid and dry sodium chloride. It was dried over phosphorus pentoxide and purified by repeated vacuum distillations. Before an experiment the reaction vessel was evacuated by a high vacuum mercury pump, was then filled with nitrosyl chloride and finally sealed off. The details of the apparatus and of the optical system will be seen from Fig. 1. The second diaphragm separated a parallel beam of light narrow enough so that all light passing through the reaction vessel fell on the light-sensitive surface of a Moll surface thermopile placed immediately behind the vessel. Two light sources were used in the present work: a 1000-watt tungsten projection lamp and a horizontal mercury quartz lamp. The thermopile–galvanometer system was calibrated by means of a standard carbon filament lamp furnished by the Bureau of Standards. Various spectral regions were isolated by means of light filters composed of Corning colored glasses and suitable solutions. The "red filter consisted of the "H. R. Red 100 per cent." glass and a ferro-ammonium sulfate solution. The "orange" filter was of the "Heat Resisting Yellow" glass and the same solution as the red filter. The "green" filter contained a didymium "G 55 P" glass, a "Sextant Green" glass and a solution containing ferric and nickel chlorides:

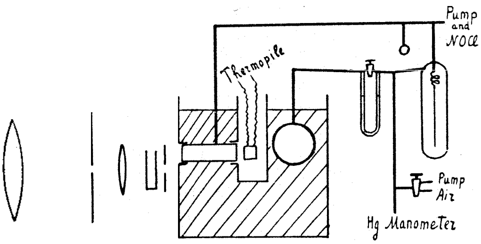

Fig. 1.

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[6] Warburg, *Sitzb. preuss. Akad. Wiss.*, 746 **(1911); 216 (1912); Kuhn, J.** *chim. phys.*, 23, **521 (1926); Bonhoeffer and Farkas, Z.** *physik. Chem.*, 134, **337 (1928).**

the “blue” filter a "Purple G 55" glass, a cuprammonium sulfate solution and a quinine sulfate solution. The "u. v." filter was a nickel oxide glass.

Results

To determine the average wave length transmitted through the filters and absorbed by nitrosyl chloride, the transmission curves of the filters as well as the absorption curve of nitrosyl chloride (at 620-mm. pressure) have been measured with a Koenig–Martens spectrophotometer. The light energy distribution in the spectrum of the tungsten lamp has been calculated assuming that the filament is at 2800° and that it emits as a gray body. By combining these three curves, the curves of Fig. 2 have been obtained which represent (in arbitrary units, not the same for different filters) the spectral distribution of light energy absorbed by nitrosyl chloride. These curves served to determine the average wave lengths used in calculations of the quantum yield. In conjunction with the mercury lamp the "blue" and the "green" filters are better than 99% monochromatic (4358 and 5461 Å., respectively), whereas in the light transmitted by the "orange" filter and absorbed by nitrosyl chloride about 90% belongs to the yellow lines 5769 and 5790 Å., 10% to the green line 5461 Å. and only very little to the red mercury lines. The ultraviolet filter, according to photographs taken with a quartz spectrograph, transmits an essentially monochromatic light of the 3650 Å. mercury line. With these filters

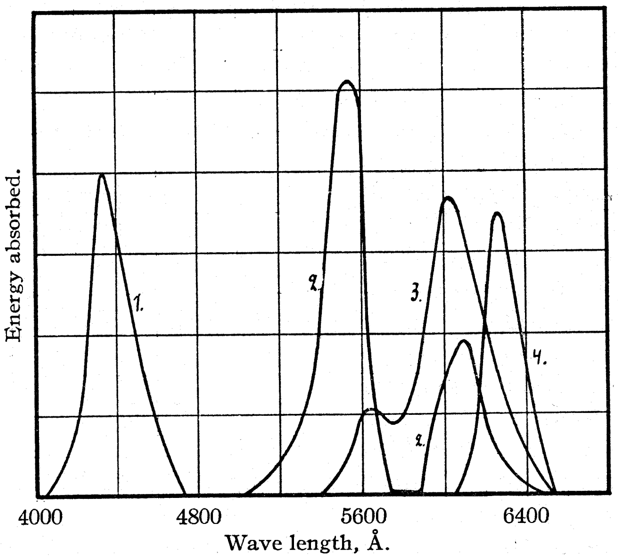

Fig. 2.—Light energy transmitted through filters and absorbed by nitrosyl chloride. 1, “Blue” filter; 2, “Green” filter; 3, “Orange” filter; 4, “Red” filter.

measurements of the quantum yield have been made and are reproduced in a summarized form in Table I. Each of the values for the decomposition rate there presented is a mean of 4 to 8 independent runs, the average deviation of the single runs from the mean amounting to about 8%. Since, in order to obtain as good a monochromasy as possible, the transmissions of the filters have been sacrificed to a considerable extent and the resulting decomposition rates were very slow, it was not possible to neglect the rate of the opposed dark reaction as Bowen and Sharp have done. Instead, the thermal reaction was measured before and after each illumination and the mean was used to correct the rate obtained on illumination. The taking of an arithmetic mean involves here an error since the thermal reaction is of the third order,[7] but the whole correction being small, this error can be neglected.

The light energy absorbed by nitrosyl chloride was determined by measuring the thermopile deflections while the vessel was alternately filled with nitrosyl chloride and emptied, the reactant being frozen out by liquid air. Considerable difficulty was experienced in the beginning since the absorption with the red filter amounted to only about 3% of the transmitted energy while the fluctuations in the lamp intensity exceeded 5% on account of the line voltage variations. This was overcome by introducing a second thermopile (a linear one of the Coblentz type) placed at some distance from the lamp and taking simultaneous readings with both thermopiles. The readings of the linear thermopile were assumed to be proportional to the lamp intensity and served to reduce the readings of the Moll thermopile to a constant lamp intensity. The values presented in Table I are the

TABLE I

QUANTUM YIELD IN THE DECOMPOSITION OF NITROSYL CHLORIDE ($T = 21.7°$)

Lamp	Filter	Wave length (mean), Å.	Gas	Mm.	Rate: Mm. Hg per hr.	Rate: Moles per sec. $\times 10^9$	Energy absorbed: Mm. on the scale	Energy absorbed: Cal. per sec. $\times 10^7$	Molecules, quanta
W	Red	6350	NOCl	615	1.49	5.61	7.3	1.13	2.2
W	Orange	6000	NOCl	615	6.39	24.2	36.1	5.58	2.0
W	Green	5600	NOCl	615	1.49	5.61	9.3	1.44	1.9
W	Blue	4350	NOCl	615	2.17	8.22	16.6	2.40	2.2
W	Blue	4350	NOCl	87	2.02	7.62	14.4	2.22	2.2
W	Red	6350	NOCl	87	0.258	0.973			
W	Blue	4350	NOCl N_2	87 606	1.89	7.17	14.4	2.22	2.0
W	Red	6350	NOCl N_2	87 606	0.250	0.945			
Hg	Orange	5760	NOCl	685	1.07	4.15	6.5	1.00	2.0
Hg	Green	5461	NOCl	685	0.54	2.05	3.0	0.46	2.3
Hg	Blue	4358	NOCl	685	1.14	4.30	8.2	1.26	2.2
Hg	U. v.	3650	NOCl	685	1.14	4.30	8.0	1.23	2.7

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[7] Trautz, Z. anorg. Chem., 97, 241 (1916); 110, 248 (1920).

means of some 15 readings each, the average deviation from the mean being about 10% with the red and less with other filters. In calculations of the absorbed light energy a correction of 20% was introduced which took care of the reflection losses on the rear plate of the reaction vessel and on a quartz plate protecting the surface of the thermopile.

The absorption spectrum of nitrosyl chloride was further investigated,[8] using a Hilger E2 quartz spectrograph and a plane grating with glass optics giving a dispersion of about 3.5 Å. per mm. in the first order.

The absorption by nitrosyl chloride was found to begin above 6300 Å. and to increase gradually toward the ultraviolet. Several fairly distinct maxima of absorption, however, have been observed. They are situated at about 5990, 4690, 3300 Å. and in the extreme ultraviolet (<2500 Å.). The spectrum consists on the long wave length side of numerous fairly distinct bands which gradually fade out, the appearance of the spectrum toward the shorter wave lengths becoming more and more continuous. In the region 4000–4500 Å., only using contrast photographic plates and particularly favorable concentration of nitrosyl chloride, the existence of bands could be established. In the ultraviolet below the absorption maximum at 3300 Å. no banded structure could be detected at all.

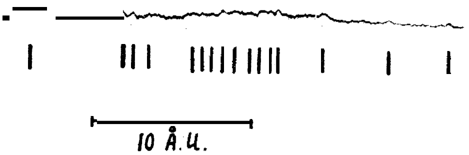

Fig. 3.

The spectrum of nitrosyl chloride thus seemed to offer the same peculiarities as the "predissociation" spectra discussed by Henri.[9] In order to ascertain this, a section of the spectrum between 4100 and 4350 Å. has been photographed in the third order of the grating, thus with a dispersion of 1.17 Å. per mm. Figure 3 is a small section of the photometer record of the plate[10] which shows that the absorption spectrum in this region has distinct line structure, although the latter is very faint. Figure 3 shows as well a reproduction of the same section of the spectrum made by hand from visual study of the plate.

Table I shows that the quantum yield observed is very near to two molecules per quantum. Indeed, if the value for the wave length 3650 Å. be excluded—we shall return to it later—the mean quantum yield is calculated to 2.1, thus a value within 5% of the theoretical 2.0. The experimental values show a slight trend to increase toward the shorter wave lengths. This is due undoubtedly to the circumstance that the correction

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[8] The author is greatly indebted to Dr. Joseph C. Elgin of this Laboratory for his valuable assistance in this part of the work.

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

[10] A Siegbahn microphotometer of the E. I. du Pont de Nemours and Co. Experimental Station, Wilmington, Delaware, has been used for the purpose.

for reflection on the glass has been applied uniformly to all values, whereas in reality the losses by reflection and scattering increase toward the ultraviolet. The value 2.7 for the 3650 Å. wave length is the only one which deviates considerably from two. Most likely this is partially due to light of this wave length being already appreciably absorbed in the thick pyrex plates forming the ends of the reaction vessel, partially to a still further increased correction for reflection and scattering. Table I further shows that the presence with nitrosyl chloride of nitrogen in a seven-fold concentration does not in the least affect the quantum yield—neither with the blue nor with the red light.

The quantum yield obtained, 2.1, is in considerable disagreement with the value 0.48 of Bowen and Sharp. The cause of this discrepancy cannot he definitely established. The neglect to take into account the dark rate could hardly account for such a large error in Bowen and Sharp's measurements and it is more likely that either in the calibration of the thermopile by Leslie cubes some mistake was made, or that the total light energy absorbed by nitrosyl chloride was determined incorrectly.

The finding of the quantum yield of two removes the necessity of introducing into the mechanism of the reaction some secondary processes reforming nitrosyl chloride. The decision must be made between the two alternate possibilities

$$\mathrm{NOCl} + h\nu \longrightarrow \mathrm{NO} + \mathrm{Cl}$$
$$\mathrm{Cl} + \mathrm{NOCl} \longrightarrow \mathrm{NO} + \mathrm{Cl_2}$$

and

$$\mathrm{NOCl} + h\nu \longrightarrow \mathrm{NOCl}^{*} \text{ (excited)}$$
$$\mathrm{NOCl}^{*} + \mathrm{NOCl} \longrightarrow 2\mathrm{NO} + \mathrm{Cl_2}$$

The observed absence of influence of nitrogen on the reaction velocity could be interpreted as favoring the first possibility but two other facts decidedly support the second scheme. The first is the indication that nitrosyl chioride can be decomposed by light energy quanta smaller than its heat of dissociation. The latter is calculated from the heat of dissociation of chlorine, 56.9 cal.,[11] and the heat of formation of nitrosyl chloride, 18 cal.,[12] to be 46.4 cal., thus corresponding to a wave length of 6130 Å., whereas in experiments wave lengths up to 6400 Å. (<44.3 cal.) were found to be effective (see Fig. *2*). More important is the evidence offered by the observations of the absorption spectrum of nitrosyl chloride. There is no doubt that this spectrum consists in the region 5500–6500 Å. of bands with line structure due to quantization of rotation. Furthermore, the plate here reproduced shows that such a structure is retained in bands of much shorter wave length. Thus, for the wave lengths employed in the present work the spectral evidence favors the formation of excited nitrosyl chloride molecules as the primary process or absorption of light energy quanta.

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[11] **Kuhn,** *Naturwissenschaften,* **14,** 600 (1926).

[12] Trautz and **Hinck,** *Z. anorg. Chem.,* *97,* 127 (1916).

The excited molecule must collide with another nitrosyl chloride molecule to yield the decomposition products.

The presence of structure in the visible absorption bands of nitrosyl chloride of course does not preclude that at shorter wave lengths the phenomenon of predissociation may not show itself. The observations recorded here rather support this supposition, although indicating that the "predissociation" state of a molecule is not necessary for its chemical activation.

Summary

1. Quantum yield measurements in the nitrosyl chloride decomposition show that the quantum yield is constant and is equal to two with wave lengths from 6300 to 3650 Å.
2. Study of the absorption spectrum of nitrosyl chloride indicates that it has banded structure throughout the visible part of the spectrum.
3. It is concluded that the mechanism of nitrosyl chloride decomposition consists in formation of an excited molecule and in a subsequent decomposition on collision.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

THE SPECIFIC HEATS OF GASES AT HIGH PRESSURES. I. METHOD AND APPARATUS AT ROOM TEMPERATURE[1]

BY NORMAN W. KRASE AND B. H. MACKEY[2]

RECEIVED JULY 22, 1929 PUBLISHED JANUARY 8, 1930

Introduction

An obvious need for data regarding the properties of gases at high pressures has made it desirable to develop a method for measuring specific heats. This is the first of a series of papers from this Laboratory reporting methods and measurements. It is confined to a description of a continuous flow, adiabatic gas calorimeter suitable for measuring specific heats up to 1000 atmospheres at ordinary temperature.

The literature contains practically no data on this important property of gases above 200 atmospheres. Holborn and Jacob[3] have published results on air but their apparatus could not be used over the entire range of pressures. An excellent review of the existing data and methods has recently been published.[4]

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[1] Submitted in partial fulfilment of the requirements for the degree of Ph.D. in Chemistry in the Graduate School of the University of Illinois.

[2] Research Assistant in Gas Engineering. University of Illinois, Engineering Experiment Station. Work of B. H. M. published by permission of the Director.

[3] Holborn and Jacob, *Berl. Ber.*, 1, *213 (1914).*

[4] Partington and Shilling, "The Specific Heat of Gases," E. Benn, London, 1924.

Experimental Method and Apparatus.—The principle of the adiabatic constant temperature flow calorimeter is well known. The present apparatus differs from previous ones particularly in the methods of measuring the several heat loss corrections.

Figure 1 is a simplified flow diagram of the method as used for nitrogen. High pressure gas storage cylinders, I, II and III are connected through a copper deoxidizer and soda lime scrubber to a thermostat. A long coil of steel tubing immersed in the liquid of the thermostat brings the temperature of the flowing gas to a constant value. Passing through a short, well-insulated tube to the calorimeter, the gas flows through the coil immersed in the calorimeter liquid. Since the temperature of the calorimeter is maintained about 6° higher than that of the thermostat, the flowing gas is heated during passage. To compensate for this continuous removal of heat by the flowing gas and for the heat losses by conduction along the steel tubing and the usual calorimeter losses, a carefully measured quantity of electrical energy is introduced into the calorimeter liquid to maintain its temperature constant. The rise in temperature of the flowing gas due to its heat absorption is measured by thermojunctions placed in the gas stream. After leaving the calorimeter the gas is expanded to about atmospheric pressure, the rate of flow being indicated by a sensitive capillary flowmeter. After humidifying the gas, the rate of flow is measured in a calibrated wet meter and the gas then is collected in a water-sealed gas holder. As needed the gas is recompressed by means of a three stage gas compressor into cylinder I and, for work at 300 atmospheres or more, is further compressed above a water piston formed by the hydraulic pump. The usual method of maintaining a constant pressure on the calorimeter was to pump cylinder III to the desired calorimeter pressure and cylinder II to a higher pressure. By adjustment of the pressure regulating valve between the two, the calorimeter pressure was held constant.

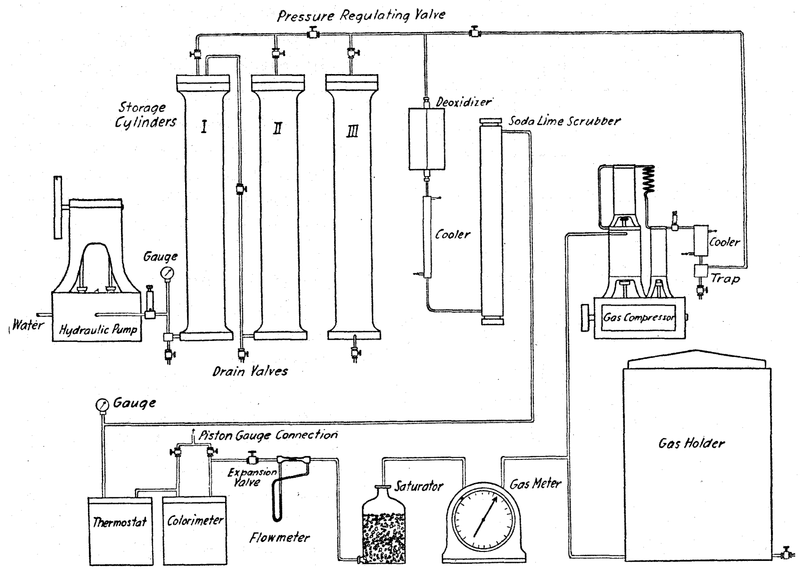

Fig. 1.

The actual manipulation during an experiment, in addition to that just described, consisted in adjusting the electrical energy input to the calorimeter so that its temperature remained constant. With a constant rate of gas flow at a constant pressure, a steady calorimeter temperature indicated that the energy input exactly equaled the energy absorbed by the gas and the energy lost by conduction, radiation, etc. Measurements of the several losses and subtraction from the total gave the energy absorbed by the gas in its passage through the calorimeter. Measurement of the gas temperature rise corresponding to this heat gives directly the heat capacity at the pressure used.

The Calorimeter.—Because the requirements to be met in this problem were radically different from any recorded in the literature, the final calorimeter as used was the result of experience and trial. An exact evaluation of the conduction losses and the measurement of the gas temperature rise offered the principal difficulties. The essential features of the calorimeter are shown in Fig. 2. A Parr adiabatic calorimeter was modified in several ways. The water jacket and cover together with the circulating pump were retained. A small resistance heater was placed in the jacket and the heat input controlled by an external resistance. The inside compartment consisted of a small copper can containing 1000 cc. of kerosene. Four feet of steel tubing, one-quarter inch in outside diameter and one-sixteenth inch bore, was coiled inside the can. By leaving a turn of tubing above the liquid the temperature gradient along the tubes leading out was reduced. The kerosene was stirred in the usual way and a resistance coil immersed in it and controlled by a sensitive external resistance furnished temperature regulation. A twelve-volt storage battery supplied a steady source of current. The jacket and calorimeter temperatures were measured by means of Beckmann thennometers.

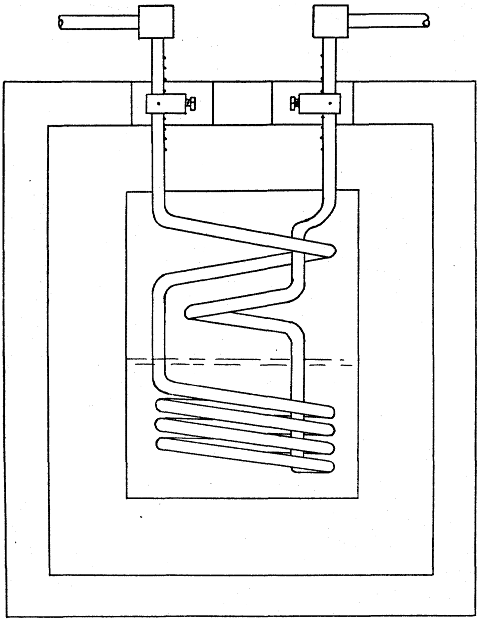

Fig. 2.—High pressure calorimeter.

The connections between the ends of the calorimeter tubing and the external tubing carrying gas into and out of the calorimeter were made by means of specially designed "gradient" tubes. These are shown in Fig. 3. The purpose of these tubes is two-fold. Since they connect the inside of the calorimeter with the outside, it is necessary to measure their temperature gradient in order to evaluate the heat conduction loss along them. They also contain the thermocouples that indicate the incoming and outgoing gas temperatures. Since the tubes are well insulated so that no heat is lost to or gained from the surroundings, any diierence in the amount of heat carried by.conduction along different sections may be accounted for as having gone into the gas. Consequently the amount of heat passing the section where the gas temperature is read is the true conduction loss. In order to introduce the "gas" couples into the stream, it was necessary to enlarge the gradient tubes at this point. The thermocouples were made from No. 40 copper and No. 36 constantan wire, double silk insulated and coated with paraffin. These wires were threaded through a small Bakelite compression cone, a steel conical disk and a nut as shown. On assembling and tightening the nut, the Bakelite was crushed around the wires, keeping them electrically insulated and sealing the opening. By connecting the constantan wires of the two gas couples together, the difference between the temperatures of the incoming and outgoing gas was read directly. This is the "rise" desired.

The temperature gradient on each side of the enlarged section was measured by similar junctions placed at the dots shown on Fig. 2. A constantan wire was placed along the outside of the tube with copper wires soldered on at known intervals. These junctions were electrically insulated from the steel by lacquer. *By* plotting the temperatures of the thermocouple points against their distance from one end, a smooth curve is obtained. The slope at any point gives the amount of heat passing that point; the heat quantity desired, however, is that passing the enlarged section containing the gas couple. The slope at one side gives the heat entering this section and the slope at the other gives that leaving; their average is taken as very close to the true value for the section.

All thermocouple readings were made using a low resistance Type HS Leeds and Northrup galvanometer and a White ten thousand microvolt single potentiometer. It was possible to estimate tenths of a microvolt from the galvanometer deflection. All switches and connections were copper and all junctions soldered. The galvanometer was mounted on a concrete pier set through the floor to eliminate vibration. The scale distance was one and one-half meters.

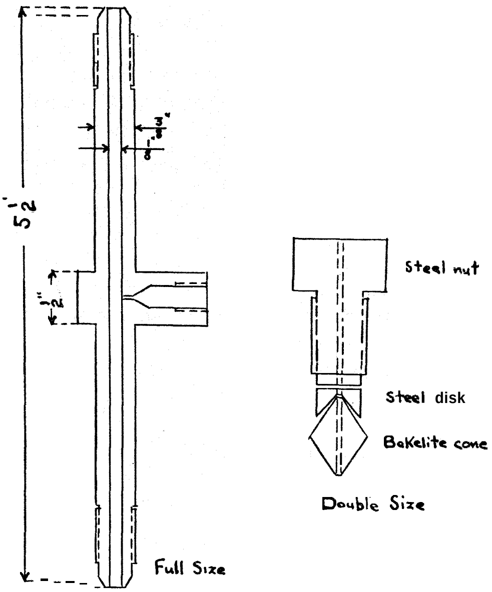

Fig. 3.—Gradient tube.

Auxiliary Measurements.—Other quantities measured during an experiment were (a) the pressure of the gas in the calorimeter tubing, (b) the pressure drop across the calorimeter, (c) the rate of flow of gas, (d) the heat of stirring and miscellaneous calorimetric loss. These measurements will be described in order.

A dead weight piston gage[5] was used as a standard and all Bourdon gages were frequently calibrated against it. Such calibrated gages were then used during experiments. The connections in the tubing at the upper end of each gradient tube permitted direct measurement of the gas pressure in the calorimeter. The piston gage is too sensitive for measurement of the flowing gas pressure and indicating gages are perfectly satisfactory. The change of C_p with pressure is greatest at low pressure and is of the order of 0.1% per atmosphere. Regulation to this accuracy is easily accomplished.

In order to measure the pressure drop of the flowing gas, a glass U-tube was connected to the two tee outlets. The use of glass is safe up to about 200 atmospheres. According to the laws of fluid flow the pressure drop for a given rate of flow of expanded

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[5] Publications from the Massachusetts Institute of Technology, *63,* No. 28, July, **1929.**

gas should decrease with pressure; the measured drop at low pressures therefore permits a calculation of the Joule–Thomson effect due to expansion in the calorimeter. The measured pressure difference at 100 atmospheres is less than one-fourth of an atmosphere. The error due to this is discussed later.

The rate of flow of gas is determined by measurements after expansion. In order to increase the sensitivity of control of the rate, a special valve was used having an extended handle. This valve was heated to counteract the cooling due to expansion since this seemed to improve the regulation. The gas then passed through a capillary flowmeter having an inclined tube to magnify small changes in head of the indicating liquid. This meter served merely to indicate constancy of rate. After humidification the gas passed through a wet meter. The rate was read with an accurate stop watch. The wet meter was calibrated immediately after each experiment under exactly the same temperature and rate conditions as obtained during the experiment. The calibration consisted in weighing a small steel cylinder containing compressed gas, expanding this gas at the same rate used during the experiment, reading the indicated volume and time interval, and re-weighing the cylinder. The weight of gas was usually about 500 grams and readily could be weighed to one gram.

The heat of stirring and the losses due to radiation, convection, evaporation, etc., are determined by making measurements with no gas flowing but with all other conditions exactly as during a regular experiment. The heat put into the calorimeter as electrical energy plus the heat put in by the stirrer exactly equal the losses due to conduction along the steel tubing and all other losses. Since the electrical energy input and the conduction loss are accurately measured, their difference is equal to the difference between the heat of stirring and the other losses. This last difference varies only slightly with room temperature and may be used as a constant of the calorimeter under normal conditions.

Typical Results

Data taken from duplicate experiments at 200 atmospheres are shown in Table I.

TABLE I

RESULTS OF TYPICAL EXPERIMENTS

			Expt. 11	Expt. 12
Absolute pressure, atm.			200	200
Room temperature, °C.			24	20
Calorimeter temperature, °C.			29.8	29.6
Thermostat temperature, °C.			22.4	21.8
Gas temperature, rise, °C.			6.80	7.60
Voltmeter reading			11.2	11.0
Ammeter reading			0.569	0.562
Wet meter reading, cu. ft. per minute			1.418	1.183
Wt. of gas passed in calibration, g.			590	674
Vol. of gas passed in calibration, cu. ft.			18	20.0
Gas flow, moles per minute, corrected			1.66	1.422
Gradient tube temp. dences °C. (enlarged section)	Inlet	Above	0.37	0.83
		Below	0.32	0.72
	Outlet	Above	0.44	0.99
		Below	0.38	0.85
Conductivity loss, calories per minute			0.4	0.9
Power input, corrected			93.2	89.9
Value of MC_p			8.25	8.31

A typical set of data for the evaluation of the heat of stirring and other corrections is given in Table **11.** The result, 2.20 calories per minute, is used to correct the power input in Table I.

TABLE II

TYPICAL SET OF DATA

Room temp., °C.	23.00
Calorimeter temp, °C.	29.80
Voltmeter reading	0.40
Ammeter reading	0.02
Power input, calories per minute	0.115
Temp. difference along inlet tube, °C.	0.86
Temp. difference along outlet tube, °C.	0.99
Cross sectional area of tubing, sq. cm.	0.633
Conductivity of tubing metal	0.110
Conduction loss inlet tube = (0.86 X 0.633 X 0.11 X 60)/3.33 =	1.08
Conduction loss outlet tube = (0.99 X 0.633 X 0.11 X 60)/3.33 =	1.24
Conduction loss (total), calories per minute	2.32
Net correction, calories per minute = 2.32 − 0.115 = 2.20	

Discussion of Errors

The reduction of the size of the errors in a problem such as this is of prime importance because approximate results have comparatively little value. A constant error would not change the relative value of the results but relative values as determined by this method would probably be inferior to those obtained from compressibility data.

The nitrogen used in these experiments was purchased from the Linde Air Products Company and was their regular grade of atmospheric nitrogen guaranteed to be better than 99% pure. The deoxidation by heated copper and drying should leave only a trace of argon present as an impurity. No analysis was made to determine the purity.

The pressure regulation was accurate to about an atmosphere during an experiment. This is about the order of the sensitivity of the gages used. These gages were calibrated frequently against the piston gage so no large error due to change in calibration was possible. The change of C_p with pressure is somewhat less than 0.1% per atmosphere change between one and two hundred atmospheres. The change is greater here than in any other interval so this error may be taken as less than 0.1%.

The voltmeter and ammeter used to measure the power input were calibrated against a Leeds and Northrup Type K potentiometer using Leeds and Northrup resistance boxes. The calibrations should be reliable to 0.1% of the full scale reading. The ammeter readings were taken at about half the scale value so an error of 0.2% might be introduced here. The voltmeter readings were usually close to the maximum scale value, so the error here would be of the order of 0.1%.

The error in the gas flow measurement can be reduced to the order of the power input error. The flowmeter reading can be held constant to 0.05% as checked against the wet meter with a stop watch. It is unlikely that any appreciable error is ever introduced due to the change in calibration of the wet meter during the experiment or between the experiments and the subsequent calibration. The flowmeter reading always has checked the wet meter reading when timed during the run and during the calibration. The weight of gas passed during calibration is usually about 500 g., accurate to one gram, so this error may be 0.2%.

The thermocouples have already been described in connection with the temperature measurements in the calorimeter. The calibration of the difference couples after being sealed into the tubes presented some difficulty. This was done by calibrating similar couples made at the same time as the difference couples. This calibration held to a tenth of a per cent. for several sets of couples, so all calculations have been made using the value found in this manner. The accuracy of the couples reading the temperature gradient along the tubes is not so important, as the quantities involved are small.

The errors introduced by the potentiometer circuit are probably small. All connecting wires are of insulated copper and the thermocouple switches are also of copper, so large parasitic thermal e.m.f.'s are improbable. The White potentiometer has an arrangement to correct for the e.m.f.'s in the potentiometer and galvanometer circuits. All difference readings can be read to a tenth of a microvolt, which is usually about 0.04% of the reading.

Conduction losses have been discussed also in connection with the calorimeter. They should introduce no larger error than 0.1 to 0.2% in the final result. The conduction losses during a run are rarely greater than 0.5 calorie per minute and it is not likely that the correction should be in error by more than 20% of this. The correction, called heat of stirring, depends for the most part on the conduction loss during a static calibration. The actual heat of stirring should be very constant, as the stirrer speed and liquid level are always the same. This correction has always been found to be 2.2 calories per minute with a variation of not more than ±0.1 calorie. If the largest variation is considered, the total result is affected by slightly over 0.1%.

A discussion of the errors in a flow gas calorimeter would be incomplete without some mention of the size of the Joule–Thomson effect due to the pressure drop in the calorimeter. At 100 atmospheres the pressure difference was less than one-fourth atmosphere for the largest flow used in regular experiments, *i.* e., 1.45 cubic feet per minute. The pressure difference decreased with an increase in total pressure when the flow remained constant and increased when the total pressure was decreased. Using Bartlett's[6] value for $-(\mathrm{d}T)/(\mathrm{d}p)H$ of 0.14 calculated from his com-

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[6] Private communication.

pressibility data at 100 atmospheres, the temperature drop in expanding through the calorimeter would be slightly less than 0.04'. When the total temperature rise is 6°, this factor causes the final result to be too high by about 0.6%. This correction is less as the pressure is increased because $-(\mathrm{d}T/\mathrm{d}p)H$ approaches zero and finally changes sign.

Faulty technic in operating the apparatus is probably the main cause for errors in the final result. An average experiment takes about four hours and all conditions should be very constant for at least half an hour before the readings are taken. This is rather difficult to do since quite frequent gas compression is necessary with the high rates used.

During a satisfactory experiment the temperature of the calorimeter does not change more than 0.01' in half an hour. A correction can be applied for a slight temperature change by taking into account the water equivalent of the calorimeter and the rate of temperature change. The water equivalent is roughly one kilogram. A 0.01' rise indicates that 10 calories have been absorbed and if the rise takes place in 30 minutes, 0.3 calorie is being absorbed per minute. This correction is usually less than 0.5%. The results are reproducible to something better than 0.5% under good conditions.

Summary

A constant temperature continuous flow adiabatic calorimeter has been described. The apparatus for measurement of the specific heats of gases at ordinary temperatures and up to 1000 atmospheres pressure is described. Typical results for nitrogen at 200 atmospheres are given together with the method of calculation.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE PICATINNY ARSENAL]

THE HEATS OF COMBUSTION AND FORMATION OF AROMATIC NITRO COMPOUNDS

BY WM. H. RINKENBACH[1]

RECEIVED JULY 24, 1929 PUBLISHED JANUARY 8, 1930

Although numerous investigators have studied the relationship existing between the constitution and thermochemical constants of organic compounds and particular attention has been paid to this relationship as regards nitro explosives, stereoisomers, homologs, etc., there still exist gaps in the values available for series of compounds and their derivatives. As the availability of such physico-chemical constants is of increasing importance and certain data of this nature were desired for use in connection with other work, it was considered desirable to make accurate determinations of the heats of combustion of a number of aromatic nitro com-

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[1] Chief Chemist, Picatinny Arsenal, U. S. War Department.

pounds and to calculate their heats of formation. For purposes of comparison and confirmation, it was decided to make similar determinations with compounds for which values have already been published.

Accordingly, calorimetric studies were made of fourteen nitro compounds

TABLE I

THERMOCHEMICAL CONSTANTS OF NITRO COMPOUNDS. HEAT OF COMBUSTION

Compound	G. cal. per g. at const. vol.	G. cal per g. mole At const. vol.	G. cal per g. mole At const. press.	Heat of formation at const. press.	Heat of nitration at const. press.
Nitronaphthalene	6878.3	1,190,400	1,190,547	−7,147	49,750
1,5-Dinitronaphthalene	5298.9	1,155,521	1,154,641	−5,441	29,670
1,8-Dinitronaphthalene	5286.1	1,152,729	1,151,849	−2,649	31,400
1,3,8-Trinitronaphthalene	4223.9	1,111,181	1,109,275	+5,725	35,275
m-Nitraniline	5463.9	754,390	754,097	+17,503	54,500
	5552	766,500[2]	766,300[2]	+12,200	49,200
2,4-Dinitraniline	3933.9	720,179	718,859	+18,541	33,240
2,4,6-Trinitraniline	2962.2	675,595	673,249	+29,951	38,310
2,3,4,6-Tetranitraniline	2411.1	658,409	655,036	+13,964	10,910
p-Nitrophenol	4900.0	681,345	680,905	+56,500	47,000
			686,500[3]	+50,900	
2.4-Dinitrophenol	3526.7	649,096	647,629	+55,571	25,970
		650,200[3]	648,700[3]	+54,500	
2,4,6-Trinitrophenol (picric acid)	2687.2	615,514	613,021	+55,979	27,310
		623,700[3]	621,200[3]	+47,800	
	2677	613,200[4]	611,900[4]	$57,100	
2-Amino-4,6-dinitrophenol	3408.3	678,490	676,877	+60,523	
p-Nitrobenzaldehyde	5250.6	793,103	792,661	$44,139	
	5306	801,500[5]	801,000[5]	+30,800	
2,4,6-Trinitrobenzaldehyde	3035.0	731,599	729,106	+34,294	
2,4,6-Trinitrotoluene (TNT)	3598.9	817,202	815,296	+16,504	29,400
	3622	822,500[3]	820,700[3]	+11,100	
	3691	838,115[7]		+13,600[7]	
2,4,6-Trinitrophenylmethylnitramine (Tetryl)	2924.4	839,566	836,486	−4,686	14,100
		844,300[3]	842,300[3]	−10,500	
	3016.5[7]	866,007		−14,200[7]	
2,4,6-Trinitro-*m*-xylene (TNX)	4039.4	973,843	971,643	+22,907	
2,4,6-Trinitroresorcinol	2202.8	539,805	537,019	+131,981	
2,4,6-Trinitro-anisole	3236.1	786,599	784,399	+47,400	
2,4,6-Trinitrochlorobenzene	2609.4	645,842	643,202	−8,400	
Hexanitrodiphenylamine	3011.7	1,322,468	1,317,628	−13,828	
m-Dinitrobenzene	4149.4	697,315	696,342	+6,858	36,000
	4155	698,300[6]	697,200[6]	+6,000	
			699,400[3]	$3,800	33,000

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[2] Swarts, Bull. *acad. Belg.,* 43 (1909).

[3] Garner and Abernethy, Proc. Roy. *Soc.* London, **99A,** 213–235 (1921).

[4] Roth and Macheleldt, "Dissertation," Braunschweig, 1921.

[5] Matignon and Deligny, *Compt.* rend., 125, 1103 (1897).

[6] Bertholet and Matignon, *ibid.,* 113, 246 (1891).

[7] Rubtzov and Sever'yanov, J. Russ. *Phys.-Chem. Soc.,* 50, 140–144 (1918)

for which no values were found in the literature, as well as of seven similar compounds of importance which had been studied by previous investigators. The data obtained are considered as serving to close a number of gaps in series of values available and hence of importance in determining the relationship between the constitutions and physical constants of chemical compounds.

Materials.—All materials used were of the highest purity, being purified by recrystallization until constant melting points agreeing with accepted values were obtained. Each compound was then kept in a sulfuric acid desiccator in a dark place until required for use.

Experimental Procedure.—A calorimeter of the Parr type was used in determining the values for heats of combustion given. This was equipped with a calibrated Beckmann thermometer and a cathetometer permitting the accurate estimation of 0.001°. The calorimeter was calibrated by means of pure benzoic acid furnished by the U. S. Bureau of Standards and found to give results accurate to ±11 calories per gram.

Duplicate or triplicate determinations were made with each material, the average value being reported. The initial temperature of the system in each case was 22 to **23°**. Combustions were carried out with the oxygen in the bomb at a pressure of 400 lbs./sq. in. **At** the completion of each combustion the bomb was rinsed out and the nitric acid formed was determined by titration, the proper correction for this being applied to the calorimetric results.

Results.—The values for heats of combustion at constant volume were determined. From these the heats of combustion at constant pressure and the heats of formation were calculated. Table I gives the constants so determined and calculated, as well as a number of corresponding values reported by other investigators.

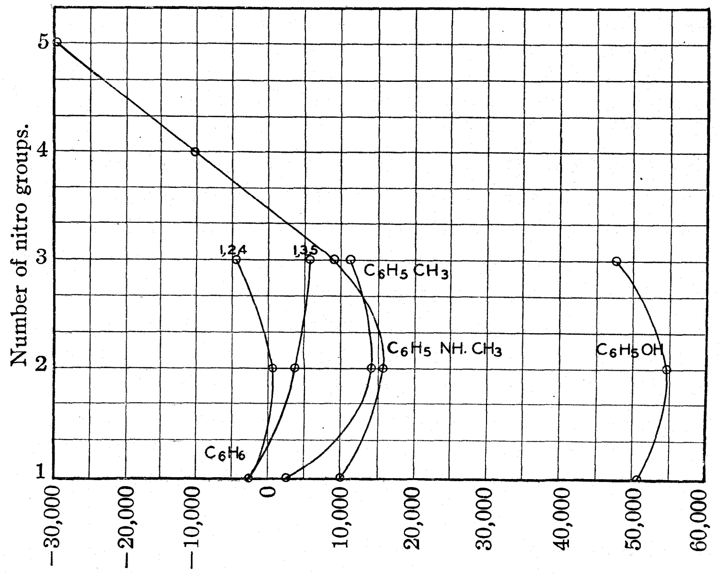
In making the calculations, the following constants were used: R = 1.9885; T = 295°K.; H_F of H_2O (liq.) = 68,400 cal./g. mole; H_F of CO_2 = 04,400 cal./g. mole; H_F of HNO_3 = 41,500 cal./g. mole.

A comparison of the values for heats of combustion determined with those previously recorded for some of the compounds would indicate a probable accuracy of about 1%. Standardization of the calorimeter indicated an accuracy of ±0.18%.

The possible error of 1% is based largely on the fact that Garner and Abernethy[3] give values from 0.2 to 1.3% (av. 0.7) higher for six compounds than those found by the writer. However, the value found for picric acid is 0.2% higher than that given by Roth and Macheleldt,[4] who also carried out their investigations quite recently. Rubtzov and Sever'yanov,[7] the only other recent investigators who have reported on two of these compounds, give results which apparently are much too high, being 2.5 and 3.1% higher than those determined by the writer and 1.9 and 2.6% higher than those reported by Garner and Abernethy. The work of the last-mentioned investigators having been done with great care, the results given by Rubtzov and Sever'yanov are at least open to question and do not form the basis of a fair comparison.

A similar comparison with values reported by other investigators shows that the determinations on check compounds herein reported are lower than those given by Swarts,[2] Matignon and Deligny[5] and Bertholet and Matignon[6] by 1.6, 1.4 and 0.1%, respectively.

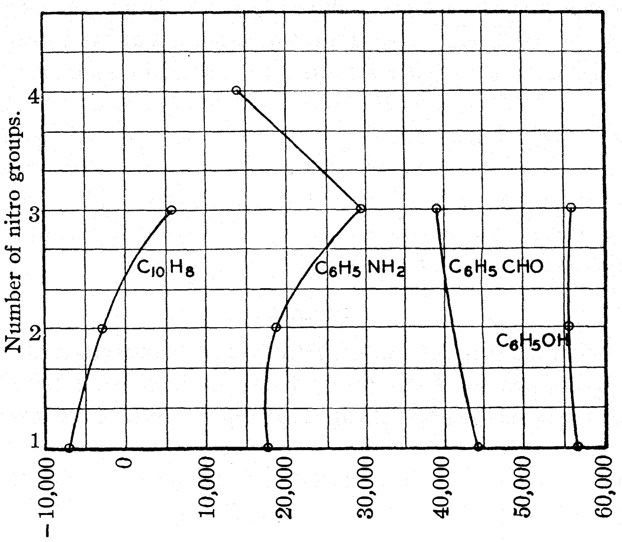
From these facts it may be concluded that the new values for heats of combustion now reported have a possible error of −0.7%, though the existence of this percentage of error instead of the ±0.18% indicated by the calibration experiments cannot be considered as proved. The insufficiency of data giving direct comparisons with at least several other investigators for individual compounds renders doubtful any rigid conclusion that the results reported in this paper contain a consistent error approximating −0.70%. This lack of comparisons is due to the fact that the filling of gaps in existent data was the prime objective of this study.



Heat of formation at constant pressure in cal./g. mole.

Fig. 1.

As is to be expected, when values for the heat of combustion of a compound determined by other investigators and the writer are used for calculating the heats of formation, the difference in results will be numerically equal but proportionally much greater than the difference in heat of combustion values. When the values for heats of formation of the compounds in each series of nitro derivatives, as calculated from the determinations of Garner and Abernethy[3] (Fig. 1) and of the writer (Fig. 2), are plotted against the number of nitro groups present in each compound, it is noted that the effect of the divergences is to produce curves having quite different orientations with respect to the reference axes.



Heat of formation at constant pressure in cal./g. mole.

Fig. 2.

If the heat of formation be used to calculate the heat of nitration (reaction) evolved when each member of a nitro compound series is prepared by nitrating the next lower nitro compound or the hydrocarbon itself in the case of the mononitro compounds, comparative results having *a* bearing on the accuracy of the combustion values determined by the writer are obtained.

TABLE II

THERMOCHEMICAL DATA

	Heat of combustion at const. press.[3], cal./g. mole	Heat of formation at const. press.. cal./g. mole	Heat of nitration, cal./g. mole
Nitrobenzene	739,700	−2,300	37,300
m-Dinitrobenzene	699,400	+3,800	33,000
1,3,5-Trinitrobenzene	663,400	+5,600	28,700
o-Dinitrobenzene	702,600	+ 600	29,800
1,2,4-Trinitrobenzene	673,700	−4,700	21,600
o-Nitrotoluene	897,200	+3,000	32,700
2,4-Dinitrotoluene	852,800	+13,200	37,100
2,4,6-Trinitrotoluene (TNT)	820,700	+11,100	24,000
p-Nitromethylaniline	924,300	+10,100	43,200
2,4-Dinitromethylaniline	884,500	+15,700	32,500
2,4,6-Trinitromethylaniline	857,900	+ 8,100	19,300
Tetryl	842,300	−10,500	8,300
p-Nitrophenol	686,500	+50,900	41,400
2,4-Dinitrophenol	648,700	+54,500	30,500
2,4,6-Trinitrophenol (picric acid)	621,200	+47,800	20,200

Values given by Garner and Abernethy (Table 11), with one exception, indicate a rather regular rate of decrease in the amount of heat given off with the introduction of each successive nitro group into the ring. In no one of the several series covered by the writer (Table I) was this found to be true, the entrance of the second nitro group in each case causing the liberation of less heat than the third. This is contrary to both theory and observed fact and is ascribable to variation in the errors in determining heats of combustion, small variations in the percentage of error causing much larger variations in derived values. This would indicate that the new determinations of heats of combustion reported in this paper are probably low to the extent of 0.7%.

Summary

1. The heats of combustion of twenty-one compounds have been determined, no values for fourteen of these having been previously published. From these, heats of formation and of nitration have been calculated.

2. Study of the values determined and calculated indicate that those determined have a probable error of −0.7%.

DOVER, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

THE EFFECT OF PH UPON THE PRECIPITATION OF ZINC AMMONIUM PHOSPHATE

BY T. R. BALL AND MEYER S. AGRUSS

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The well-known method of determining zinc as zinc ammonium phosphate was first introduced by Tamm.[1] It has been studied by several investigators[2] with the final result that the precipitation is carried out in neutral or faintly acid solution, using diammonium phosphate as the precipitant. From five to twenty grams of ammonium chloride is present in the solution and the amount of precipitant may vary from ten to twenty times that of the weight of zinc estimated to be present. The precipitate formed at first is assumed by Olsen[3] to be amorphous $Zn_3(PO_4)_2$, which in the presence of ammonium salts is changed into crystalline Zn-

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[1] Tamm, *Chem. News,* 24, 148 (1871).

[2] Lösekann and Meyer, *Chem.-Ztg.,* 10, 729 (1886); M. Austin, Am. J. *Sci.,* *8,* 206, 1899; *Z. anorg. Chem.,* 22, 212 (1900); Langmuir, *Chem. News,* 79, 183 (1899); Dakin, *Z. anal. Chem.,* 39,273 (1900); Voigt, *Z. angew. Chem.,* 22,2282 (1909); Langley, THIS JOURNAL, 31, 1051 (1909); Finlay and Cumming, J. *Chem. Soc.,* 103, 1004 (1913); see also Dede, *Ber.,* **61,** 2463 (1928).

[3] Olsen, "Quantitative Chemical Analysis," D. Van Nostrand Co., New York. 1904, p. 82.

NH_4PO_4 by hot digestion. Practice varies as to the method of washing the precipitate, some authors using a 1% solution of diammonium phosphate followed by a mixture of water and alcohol. Langley[2] finds that washing with cold water gives satisfactory results.

While the accepted procedure calls for precipitation in a neutral or faintly acid solution, none of the previous investigators has determined the optimum PH. Fales[4] states that "the exact value of Pa for which zinc ammonium phosphate is least soluble has not been definitely ascertained, but apparently is around a value of Pa = 7.5." The present work has to do with the determination of the optimum PH.

Materials and Procedure

A high grade of zinc sulfate was mixed with C. P. ammonium sulfate mole for mole, dissolved in boiling water and twice recrystallized from hot water. The crystals were air-dried and analyzed by gentle ignition to $ZnSO_4$ in a large platinum crucible. The percentage of $ZnSO_4$ was found to be 40.19, 40.15 and 40.18% in three determinations; average, 40.173%; calcd. for $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ = 40.193%. A standard was made by dissolving the salt in a weighed amount of water and all samples were taken by weighing the solution. In general, 5 g. of ammonium chloride and 10 cc. of 2 N sodium acetate were added to each zinc solution, followed by dilution to 140 cc. The solutions were then placed on a water-bath and when hot 10 cc. of 10% diammonium phosphate was slowly added from a pipet. The diammonium phosphate used conformed to the specifications of the Committee on Analytical Reagents of the American Chemical Society.[5] A solution of 1 g. in 10 cc. of water was colored pink by the addition of 2 drops of phenolphthalein solution. After two hours on the water-bath in a covered beaker, the precipitates were filtered onto Gooch crucibles, washed with about 150 cc. of cold water, 5 cc. of 95% alcohol and dried in the oven for one hour at 105°. The amount of zinc was then calculated on the assumption that the precipitate was $ZnNH_4PO_4$. In some cases larger amounts of ammonium chloride were added, as shown in the notes to Table I.

Where low Pa values were desired, varying amounts of 1.0 N HCl were added just before the addition of the precipitant. To produce high PH values, 1.0 *N* NaOH or 10% NH_3 was added. All of these reagents were carefully tested and found to yield no precipitate with phosphate under the range of conditions used.

The PH values of the undiluted filtrates were determined with a hydrogen electrode against a normal calomel. This was the method followed for all the results shown in Table I which were obtained by Ball. Mr. Agruss followed much the same procedure except that he used an equivalent amount of ammonium acetate in place of sodium acetate and determined the PH by the Gillespie drop ratio method, using the Clark and Lubs indicators. The results of Mr. Agruss, forty-seven in number, are not given in the table since they are so consistent with those of the senior author that their inclusion would add nothing to the interpretation. They simply show that the presence of sodium salts, in the concentrations used,

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[4] Fales, "Inorganic Quantitative Analysis," The Century Co., New York, 1925, p. 257.

[5] *Ind. Eng. Chem.*, 19, 645 (1927).

are without effect. The object of adding the sodium acetate was to increase the buffer action.

Experimental

The results are given in Table I, which is self-explanatory. Unless otherwise stated each solution contained 5 g. of ammonium chloride. The average error for each PH value is plotted against the *P*H in Fig. 1.

TABLE I

EFFECT OF *P*H ON THE PRECIPITATION OF ZINC AMMONIUM PHOSPHATE

5 g. of NH_4Cl; 1 g. of $(NH_4)_2HPO_4$; 10 cc. of 2 N $NaC_2H_3O_2$; final volume, 150 cc

No.	Zn taken, g.	Zn found, g.	Error, mg.	PH	No.	Zn taken, g.	Zn found, g.	Error, mg.	*P*H
1	0.0881	0.0798	−8.3	4.2"	19	0.0726	0.0726	0.0	6.6"
2	.0883	.0855	−2.8	4.7"	20	.0363	.0363	.0	6.7
3	.0877	.0874	−0.3	5.1^a	21	.0263	,0266	+ .3	6.7
4	.0882	.0878	− .4	5.2"	22	.0717	.0716	− .1	6.7
5	.0880	.0876	− .4	5.4"	23	.0900	.0900	.0	6.9
6	.0877	.0876	− .1	5.4^a	24	.0817	.0818	+ .1	6.9
7	.0887	.0883	− .4	6.2"	25	.0834	.0834	.0	7.1^d
8	.0882	.0879	− .3	6.2"	26	.0851	.0852	+ .1	7.1^d
9	.0888	.0888	.0	6.4^b	27	.0888	.0891	+ .3	7.1^d
10	.0885	.0887	+ .2	6.4^b	28	.0892	.0894	+ .2	7.3^d
11	.0884	.0882	− .2	6.4^b	29	.0885	.0887	+ .2	7.4"
12	.0889	.0890	+ .1	6.4^b	30	.0882	.0884	+ .2	7.6^d
13	.0897	.0897	.0	6.4	31	.0892	.0896	+ .4	7.6^d
14	.0898	.0899	+ .1	6.4	32	.0876	.0878	+ .2	7.7^d
15	.0887	.0884	− .3	6.4	33	.0883	.0863	−2.0	7.8"
16	.0447	.0447	.0	6.5	34	.0887	.0844	−4.3	7.9"
17	.0183	.0181	− .2	6.5	35	.0884	.0793	−9.1	8.3"
18	.0548	.0548	.0	6.6					

[a] HCl added. [b] 10 g. of NH_4Cl. [c] 8 g. of NH_4Cl. [d] NaOH added. [e] 10% NH_3 added.

Discussion

Determinations 1 to 8 of Table I show that all results are low up to a PH of 6.2 and fall off very rapidly below 5.1. From a PH of 6.4 to 6.9 (Nos. 9 to 24) seven results show *a* zero error, five show slightly high results and four are low. The mean deviation from the theoretical over this range is zero. From a PH of 7.1 to 7.7 all results are high, with the exception of No. 25, but the error is not large. It should be noted, however, that whenever the PH exceeds **7.0,** the precipitates are removed from the beaker with great difficulty and do not have the definite crystalline structure characteristic of those precipitated from the more acid solutions. Above **a** PH of 7.7 the zinc error is negative and very large. This is obviously due to the formation of a complex ion of zinc with free ammonia. Even at PH values as low as 6.6 the odor of ammonia is distinct from the hot solution.

A study of Fig. 1 shows that the curve crosses the zero axis at 6.6. This obviously is the optimum *Ph* at which to make the determination. The results of Mr. Agruss, using ammonium acetate in place of the sodium salt, when similarly plotted, lead to the same conclusion.

The filtrates of Expts. 9 to 15, Table I, all showed a *Ph* of 6.4 regardless of the fact that Nos. 9 to 12 contained twice as much ammonium chloride as the others. The range of 6.4 to 6.9 in **Ph** shown in Nos. 13 to 24, which were all run with identical reagents, is doubtless due to variations in air circulation resulting in unequal volatilization of ammonia during the heating. However, all fall within a safe *Ph* range, so that the conclusion seems justified that the two-hour heating period in a covered beaker automatically adjusts the acidity to the proper range. This was further investigated by preparing a solution containing 5 g. of NH_4Cl, 10 cc. of 2 N NaAc and 10 cc. of 10% $(NH_4)_2HPO_4$ in a total volume of 150 cc. The *Ph* of this solution was 7.5 but it dropped to 6.9 after two hours of heating on the bath. Ten minutes of vigorous boiling, followed by dilution to the original volume with water, reduced the *Ph* to 5.6. Obviously the solution should not be boiled.

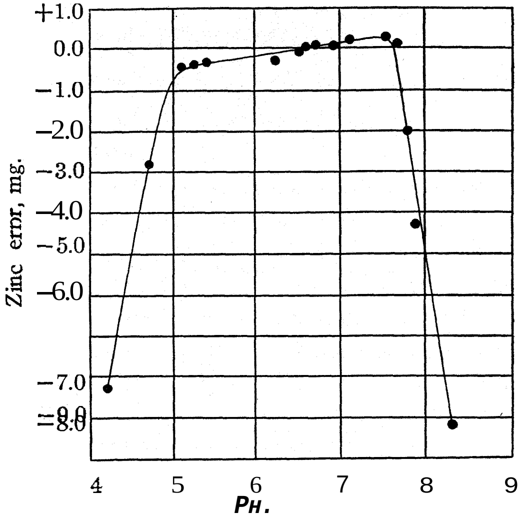

Fig. 1.—The effect of *Ph* upon the precipitation of zinc ammonium phosphate.

Justification for the addition of sodium acetate to improve the buffer action is shown by the fact that the original solution referred to above was changed from a *Ph* of 7.5 to 6.5 by the addition of 5 cc. of 1.0 N HCl. When the sodium acetate was left out the *Ph* changed to 6.3, which is dangerously low (see Nos. 7 and 8 of Table I).

Summary

1. Satisfactory results may be obtained for the determination of zinc as zinc ammonium phosphate over a Ph range of 6.4 to 6.9.
2. The optimum Ph is 6.6.
3. The concentration of ammonium chloride between five and ten grams per 150 cc. is without appreciable effect.
4. The precipitate is not crystalline at Ph values above 7.0 and is removed from the beaker with difficulty.

5. Below a PH of 5.1 and above 7.7 the results are much too low.

6. Solutions containing 5 to 10 g. of NH_4Cl, 10 cc. of 2 N $NaC_2H_3O_2$ and 10 cc. of 10% $(NH_4)_2HPO_4$ in 150 cc. have a PH of 7.5 but automatically fall to a range of 6.4 to 6.9 on the water-bath when heated for two hours.

7. Washing of the precipitate with cold water seems to yield satisfactory results.

ST. LOUIS, MISSOURI

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 228]

THE QUANTUM YIELD IN THE PHOTOCHEMICAL DECOMPOSITION OF HYDROGEN AZIDE

BY ARNOLD O. BECKMAN AND ROSCOE G. DICKINSON

RECEIVED JULY 27, 1929 PUBLISHED JANUARY 8, 1930

Introduction

In a previous paper[1] it has been shown that gaseous hydrogen azide, HN_3, is decomposed by ultraviolet radiation of wave length less than 2200 Å. The products of the reaction were found to be hydrogen, nitrogen and ammonia (ammonium azide); no hydrazine was found.

The decompositions of aqueous solutions of HN_3 by ultraviolet radiation has been studied by Gleu[2] who found that here the products were largely hydroxylamine and nitrogen with small amounts of ammonia and traces of hydrazine.

The present paper is concerned with the quantum yields in the decomposition of gaseous HN3 produced by monochromatic radiation, and with the effect of pressure on these yields.

Apparatus and Procedure

A diagram of the apparatus is shown in Fig. 1. Anhydrous gaseous HN_3, prepared as before' from sulfuric acid and NaN_3, was stored in the 1-liter bulb, A, which was attached to a vacuum system. Attached to the same system were a quartz reaction vessel, N, in which the HN_3 was irradiated, a McLeod gage, and a quartz fiber gage, H. With the mercury cut-off, C, and the cock K closed and with the cut-off M open, a desired quantity of HN_3 was admitted to the system with the aid of the doser, B. The HN_3 was frozen out by applying liquid air at P and any traces of non-condensable gas were pumped off. The cut-off M was then closed and the liquid air removed from P allowing the HN_3 to vaporize into the reaction cell, N. The pressure of the HN_3 was read from the difference in the mercury levels in the two arms of M. In those cases where the pressure of HN_3 was too small to be measured satisfactorily in this manner, this procedure was slightly modified to permit the measurement of the HN_3 pressure on the McLeod gage. The reaction cell, N, was a quartz cylinder 2.5 cm. in diameter and

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[1] Beckman and Dickinson, THIS JOURNAL, 50, 1870 (1928).

[2] Karl Gleu, Ber., 61, 702 (1928).

4.8 cm. long with flat windows fused on each end; it was attached to the rest of the apparatus through a graded seal.

After irradiation liquid air was again applied at P, the cut-off M opened and the non-condensed gas allowed to expand into the evacuated McLeod gage and quartz fiber gage. The McLeod gage reading gave the total pressure of hydrogen and nitrogen produced and this combined with the known volume of the gases (all mercury levels were held at definite marks) gave the total number of moles of nitrogen and hydrogen produced. The fiber gage readings were used to determine the mole fraction of hydrogen in the gas in the way already described.'

The source of radiation was an aluminum spark. Aluminum was used because it gives quite intense lines which are widely separated in the desired region, permitting the use of wide slits in the monochromator. The electrodes were 0.25 inch aluminum rods with the ends turned down to a diameter of 0.1 inch for a distance of $^3/_{16}$ of an inch. The small ends were essential to keep the spark from drifting about; the larger shanks were necessary to keep the tips from melting. As the electrodes eroded their separation was adjusted to a constant value of about 6 mm. during operation with the aid of an image of the spark projected upon a screen by a lens, in a manner similar to that described by Warburg.[3] The spark was operated from the 13,000 volt secondary winding of a transformer, the primary current being 40–60 amperes at 220 volts. A 0.1 mf. condenser was placed in parallel with the spark.

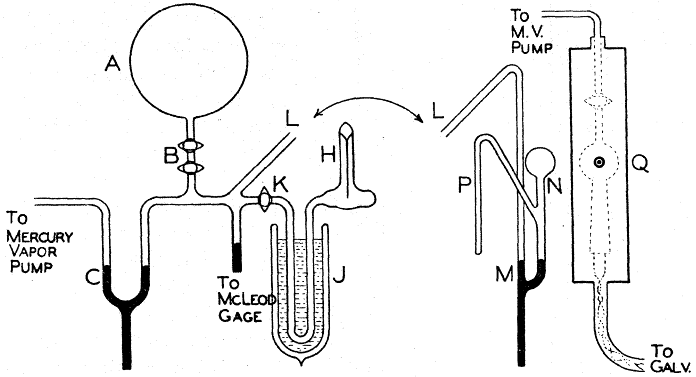

Fig. 1.—Schematic diagram of vacuum system.

The spark was placed close to the entrance slit of a Bausch and Lomb quartz monochromator. To permit this, the regular slit mechanism was replaced by a more compact one covered by a micarta cap with a rectangular hole in front of the slit. Provision was also made for blowing the spark by a blast of air issuing from the hole in the micarta cap. A shutter was also built into the monochromator.

The flux of radiation was measured by the vacuum thermocouple Q (Fig. 1), which is shown in greater detail in Fig. 2. The thermo-elements were pure bismuth and an alloy of 95% bismuth with 5% tin. The junctions were cemented to the rear faces of two circular vanes of aluminum foil. The vanes were 5.5 mm. in diameter, just large enough to receive the entire beam of radiation which was converged onto the receiving vane by a quartz lens of 2.5 cm. focal length fastened to the monochromator just outside the rear slit. The front surfaces of the vanes were coated with lampblack from a sooty flame. To aid in alignment, a piece of fluorescent uranium glass was placed imme-

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[3] Warburg, *Sitz. Ber. Preuss. Akad.*, 216 (1912).

diately behind the vanes. When in use, the thermocouple vessel was continuously evacuated with a liquid-air trap placed between it and the pump. The thermocouple was connected with a Leeds and Northrup high sensitivity galvanometer; the thermocouple, galvanometer and leads were carefully shielded in a grounded metallic covering. The front windows of the thermocouple vessel and reaction cell were aligned horizontally and both located in a plane perpendicular to the exit beam of the monochromator. The monochromator, with the spark rigidly attached to it, was arranged to slide horizontally in V-grooves provided with stops so adjusted that when the monochromator was in one extreme position, the light was focused exactly on one receiving vane of the thermocouple and when in the other extreme position, the light was centered on the reaction cell. Reaction exposures were usually about fifteen minutes long. Ordinarily measurements of the energy flux were alternated with the reaction exposures and carried over about the same time interval; during this interval a number of galvanometer readings were made with the shutter open and closed and the deflections averaged. The mean values of several such sets of readings taken successively fluctuated about 10%. It would evidently be better so to arrange the apparatus that thermocouple readings could be made simultaneously with the reaction; apparatus is now being constructed which will permit this in the study of other reactions.

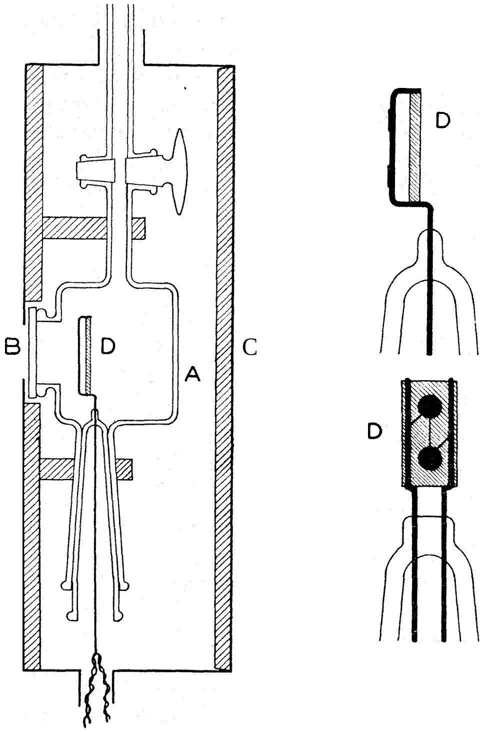

Fig. 2.—Side view of vacuum thermocouple. The thermocouple vessel, A, was of pyrex with a quartz window, B, fastened on with sealing wax. The rear side, C, of the metal-covered housing was removable for aligning. The thermocouple assembly and fluorescent screen, D, are shown in greater detail on the right.

The thermocouple–galvanometer combination was calibrated with the aid of a carbon lamp which had itself been calibrated by the Bureau of Standards. The procedure was as follows: with the aid of a Moll thermopile the transparency of a quartz plate for radiation from the standard lamp was measured and found to be 90.6%. The vacuum thermocouple was then assembled using this quartz plate as a window, and evacuated. A hole 4.50 mm. in diameter (area, 15.87 mm.^{2}) was made in a thin sheet of metal. The hole was placed in front of the thermocouple window in such a position that light from the standard lamp passing through the hole was entirely intercepted by the receiving vane; the scale deflection was 4.766 cm. (average). From the calibration of the standard lamp, the intensity of radiation at the hole was known to be 7.04 ergs per mm.^{2} per sec. Accordingly 1 cm. of scale deflection corresponded to $7.04 \times 15.87 \times 0.906/4.766 = 21.25$ ergs per second of radiation falling on the receiving vane. An exactly similar plate of quartz was used for the front window of the reaction cell. Hence, in using the thermocouple to measure ultraviolet radiation, no correction for the transmission loss at the front window of the reaction cell was necessary, *i. e.*, **1** cm. of scale deflection was taken to indicate **21.25** ergs per second entering the reacting substance To test the integrating ability of the thermocouple vane, a beam of light about **0.5** mm. in diameter was directed onto the center and then onto regions near the edge of the vane, and the deflections were noted. The deflections differed from each other by less than 1%.

Light Absorption Coefficients.—In the determination of the quantum yields it was necessary to know the absorption coefficient of HN_3 for the radiation used. Absorption coefficients were determined photographically by a method substantially the same as that described by Winther.[4] This consisted in photographing on the same plate with a quartz spectrograph a series of exposures of the radiation from the aluminum spark. **The** exposures were all of the same length and in every case the radiation passed through the reaction vessel. In half the exposures the reaction vessel contained HN_3 at a measured pressure; in the alternate exposures, the reaction vessel was empty, and calibrated wire screens of known transmission were interposed in the optical path. The plates were photometered using the microphotometer of the Mount Wilson Observatory. The resulting absorption coefficients, a, defined by the equation $I/I_0 = e^{-\alpha l}$ where I/I_0 is the fraction of radiation transmitted by a thickness of 1 cm. of gas at 0° and 1 atm., are shown in Pig. **3.** The absence of any systematic variation of a with the pressure is evidence that Beer's law holds here at least approximately.

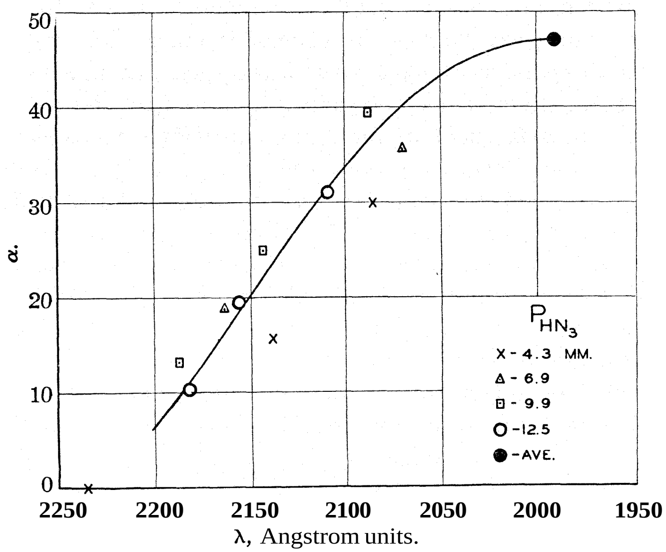

Fig. 3.—Light absorption coefficients, α, of HN_3 at various wave lengths, λ.

[4] Winther, Z. *wiss.* **Phot., 22, 125 (1923).**

Experimental Results

The results of the quantum yield determinations made with the aluminum line λ1990 are given in Table I. In the first column is given the initial pressure of HN_3 in the reaction chamber; in no case was more than 1.7% of the HN_3 decomposed. In the second column is A, the fraction of the incident radiation absorbed, calculated from the absorption coefficient $\alpha = 47.0$, assuming Beer's law to hold and allowing for reflection at the rear window of the reaction cell. The exposure time, t, is given in seconds in the third column. The variability of the galvanometer deflection, d, given in the fourth column arises in part from the fact that the slit widths and spark lengths were not the same in all experiments. The volume of the gas during the reaction was **25.3** cc. in all experiments. The volume of the products when expanded into the gages was larger, and is given in Col. 6; this volume is an effective one determined by air expansion with liquid air at P as in the measurement of the non-condensable gas pressures. The pressure of the non-condensed products given in Col. 7 came directly from McLeod gage readings. From these and the values of $\Sigma p \sqrt{M}$ determined with the quartz fiber gage, the mole fractions of hydrogen given in Col. 8 were computed. These mole fractions are, in the present case, very sensitive toward small errors in the readings of either gage. Since the measured pressures are small, we do not feel certain that the rather considerable variability of these mole fractions is real; fortunately, the quantum yields are not sharply dependent upon them. In the ninth column, the number of quanta of radiation absorbed by the HN_3 was computed from the relation

$$N_Q = \frac{21.25 \cdot d \cdot t \cdot A}{hc/\lambda} = 2.150 \cdot 10^{12} \cdot d \cdot t \cdot A$$

the factor 21.25 being the number of ergs per second of radiation entering the gas for a galvanometer deflection of 1 cm. In the tenth column is given N_{HN_3}, the number of molecules of HN_3 decomposed; this was calculated from the following equation which may be simply obtained from the perfect gas law and the consideration that the number of gram atoms of hydrogen and nitrogen in the products (H_2, N_2 and HN_3) must equal the number of gram atoms of hydrogen and nitrogen in the decomposed HN_3

$$N_{HN_3} = \frac{N \cdot p_{H_2 + N_2} v}{760RT} (3/4 - x_{H_2})$$

Here N is the Avogadro number, and R has the value 82.1-cc. atm. per degree.

The quantum yield tabulated in the last column is the ratio of the number of molecules of HN_3 decomposed to the number of quanta absorbed, *i.* e., N_{HN_3}/N_Q. The yield at the lowest pressure is regarded as less reliable than the others, partly on account of the comparatively small pressure of the products; any uncertainty in the absorption coefficient would also have its greatest effect in this run. If this run be left out of account, there remains certainly no considerable variation of yield with pressure over the range from 2 to **130** mm. The mean of all the yields excluding the first is **2.97 ± 0.45.**

TABLE I

QUANTUM YIELDS FOR THE WAVE LENGTH λ1990

Pressure of HN_3 P_{HN_3}, mm.	Fraction of light sbs., A	Exposure time, t, sec.	Galv. defl., d, cm.	Temp. of prods., T, °A.	Vol. of prods., $V_{H_2+N_2}$, cm.³	Press. of prods., $p_{H_2+N_2}$, mm. $\times 10^3$	Mole fraction of H_2, x_{H_2}	No. of quanta abs., N_Q $\times 10^{-15}$	Molecules of HN_3 decomp., N_{HN_3} $\times 10^{-15}$	%'' yield, Y
0.328	0.096	2430	4.58	298	165.0	1.22	0.152	2.26	3.92	1.74
1.93	0.441	1620	6.68	295	174.2	8.05	.161	10.15	27.2	2.68
3.26	0.620	1290	5.12	298	165.0	4.67	.110	8.71	16.1	1.84
9.4	0.934	900	7.46	295	174.2	11.17	.180	13.35	36.5	2.74
24.2	1.00	900	4.74	299	165.0	6.27	.102	9.08	21.9	2.41
27.5	1.00	900	4.92	295	174.2	7.47	.123	9.40	26.9	2.86
39.5	1.00	600	4.51	299	165.0	5.30	.080	5.75	19.1	3.32
42.0	1.00	900	5.88	295	174.2	8.62	.157	11.25	29.4	2.62
58.0	1.00	900	4.71	295	174.2	10.18	.150	9.02	35.1	3.89
71.0	1.00	900	4.63	297	165.0	8.34	.067	8.86	30.7	3.47
72.5	1.00	600	4.51	299	165.0	4.97	.052	5.75	18.6	3.23
101.0	1.00	900	4.74	299	165.0	8.58	.077	9.08	31.0	3.41
131.0	1.00	900	4.74	300	165.0	7.99	.075	9.08	28.9	3.18

The conclusion that the quantum yield is largely independent of the pressure is borne out by the results of some rate experiments made at lower pressures. In these experiments the monochromator was removed. The cell was exposed to the full radiation of the spark which was placed at a distance of 40 cm. from the cell. The spark length was controlled as before. A series of 2-minute exposures was made at various HN_3 pressures of from 0.06 to **0.5** mm. The HN_3 pressures were measured on the McLeod gage. It was found that the manipulation of the gage produced traces of decomposition; consequently, after HN_3 had been admitted to the McLeod gage and the reaction cell, the trap M (Fig. 1) was just closed and the gas in the McLeod gage pumped off after the HN_3 pressure measurement. After exposure, liquid air was applied at P, and the pressure of the non-condensed gas measured with the McLeod gage. It was also found that illumination of the reaction cell with the full radiation of the spark produced gas pressure at the rate of 6×10^{-5} mm. per minute even when the cell was empty. Consequently 12×10^{-5} mm. was subtracted from the measured pressures. The results are shown in Fig. **4** in which the abscissas are the HN_3 pressures and the ordinates the total corrected pressures of non-condensed gas. The curve has been drawn as a straight line through the origin and is evidently reasonably representative of the points.

In these rate experiments the absorption of λ1990 was sufficiently low **(13%)** at even the highest pressure, so that it could be taken as proportional to the pressure. If this is true also of such shorter wave-length radiations from the spark as may have reached the reaction cell, then the linearity of rate with pressure is evidence in favor of constancy of quantum yield down to those lower pressures.

Discussion

The first question involved in the consideration of the mechanism of photochemical HN_3 decomposition is the nature of the primary process, *i. e.*, whether light absorption is accompanied by the production of an HN_3 molecule in an excited electronic state or is accompanied by dissociation of the absorbing molecule. Unless we have to deal here with unusually large molecular diameters or with an electronic state of considerably longer life than that usually assumed ($\sim 10^{-7}$ sec.), the experiments are decidedly in favor of primary dissociation; taking a collision diameter of 5 X 10^{-8} cm., the mean time between collisions is readily calculated from the usual kinetic theory formula to be about 7 X 10^{-7} sec. at a pressure of 0.1 mm. so that a decided falling off in rate could be expected at even higher pressures, were the primary process one of excitation.

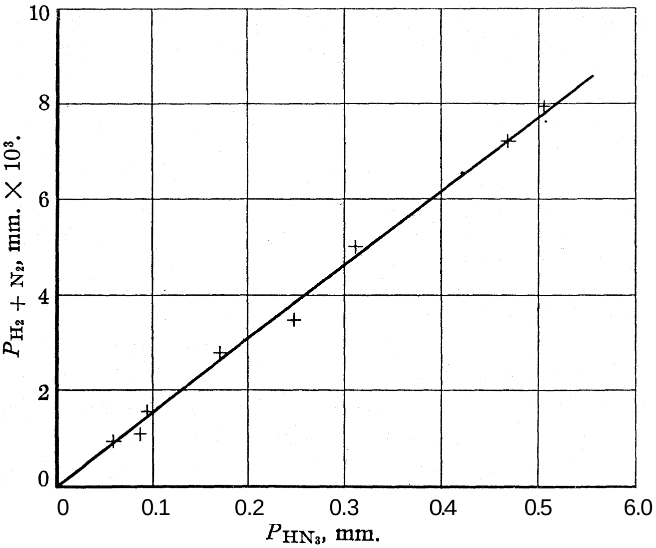

Fig. 4.—Rate of production of non-condensable gas at low HN_3 pressures.

The energy available for primary dissociation is large; a quantum of wave length λ1990 corresponds to 143,000 cal. per mole and in addition HN_3 is itself endothermal to the extent of 54,500 cal. per mole.[5] Because of the high heat of dissociation of nitrogen,[6] 219,000 cal. per mole, the

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[5] According to Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, p. 334, the heat of formation of HN_3 in aqueous solution is –61,600 cal. while the heat of solution is –7080 cal.

[6] R. T. Birge, *Nature*, 122, 842 (1928).

available energy is not sufficient for complete dissociation of HN_3 into atoms, but is sufficient for dissociation into H, N and N_2 or, it seems reasonable to suppose, into other configurations such as HN and N_2.

The fact that NH_3 is produced from HN_3 seems to require either (1) the occurrence of multiple collisions involving an active configuration (such as a collision of $2HN_3$ with one H), or (2) the transient occurrence of intermediate compounds. In the first case we should expect the amount of ammonia produced (as compared with the amount of hydrogen produced) to fall off greatly with decreasing pressure. As this appears not to be the case, we are disposed to accept the second alternative.

A possible mechanism of the reaction is the following, the first step of which is identical with that assumed by Gleu[2] to account for the formation of hydroxylamine in aqueous solution.

$$h\nu + HN_3 = HN + N_2 \qquad (1)$$
$$HN + HN_3 = H_2N_2 + N_2 \qquad (2a)$$
$$HN + HN_3 = H_2 + 2N_2 \qquad (2b)$$
$$H_2N_2 + HN_3 = NH_3 + N_2 \qquad (3)$$

If Reaction 2a went three times as often as Reaction 2b the quantum yield would be 2.75 HN_3 decomposed per quantum and the mole fraction of hydrogen in the non-condensed gas would be 0.08; the averages of the observed values are 2.97 ± 0.45 and 0.111 ± 0.036, respectively. However, we do not care to stress this particular mechanism; indeed, we regard the ad *hoc* invention of intermediate compounds as a pastime usually indulged in with more entertainment than profit.

We would finally draw attention to the fact that in spite of the very high concentration of energy involved in the primary process and the highly explosive character of HN_3, there is no discernible tendency toward chain reaction even at a pressure of 130 mm. This behavior is, however, not entirely unprecedented, for low quantum yields have been found in the decomposition of the gaseous compounds chlorine monoxide[7] and azomethane,[8] both of which are explosive.

Summary

Using monochromatic radiation of wave length λ1990, quantum yields in the decomposition of gaseous HN_3 have been measured over a pressure range of from 2 to 130 mm.; the quantum yield was found to be substantially constant over this range with the average value **3.0** ± 0.5 molecules of HN_3 decomposed per quantum absorbed. At pressures of from 0.06 to 0.5 mm., the rate of decomposition produced by the full radiation from an aluminum spark was found to be proportional to the HN_3 pressure, indicat-

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[7] E. J. Bowen, J. *Chem. Soc.,* 123, 2328 (1923); Bodenstein and Kistiakowsky, *Z. physik Chem.,* 116,371 (1925).

[8] H. C. Ramsperger, THIS JOURNAL, 50,123 (1928).

ing constancy of yields also over this pressure range. Some features of the mechanism of the reaction are discussed.

PASADENA, CALIFORNIA

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

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. XI. THE OXIDATION OF ORGANIC ACIDS

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Introduction

The permanganate oxidation method for a number of organic acids[1] such as tartaric, malic, malonic, etc., is not entirely satisfactory, due to the fact that formic acid, which is one of the oxidation products, is, in turn, slowly oxidized by permanganate in acid solution. If a direct titration of any of these acids with standard permanganate in hot solution is attempted, the end-point is unsatisfactory, and if even a slight excess of standard permanganate is added, followed by excess of standard oxalic acid and back titration with permanganate, some formic acid is oxidized, the amount depending on such factors as concentration of the formic acid, amount of permanganate in excess and time of its action, temperature and acidity of solution. Therefore, even fairly accurate results can be obtained only when experimental conditions are closely controlled. To avoid the error caused by oxidation of formic acid, the complete oxidation of a number of these acids to carbon dioxide and water has been proposed, first in acid, then in alkaline solution, using standard permanganate, followed by addition of sulfuric acid, excess of standard oxalate and back titration with permanganate.

Hatcher and West[2] found that formic acid was an intermediate oxidation product in the oxidation of complex organic acids and that the rate of its oxidation by permanganate was inversely proportional to the hydrogen-ion concentration of the solution.

Benrath and Ruland[3] studied the velocity of reaction of ceric sulfate with a number of organic compounds. They were interested in determining the course of the reactions, however, rather than in an analytical method for these acids. They stated that sulfuric acid retarded the velocity of oxidation by ceric sulfate, and that a solution containing ceric

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[1] Representative references are given under the individual acids. It is obvious, however, that space is not available for complete lists of oxidation methods for determining these acids. The authors have made no attempt to prepare such a bibliography, which would be beyond the scope of the present paper.

[2] Hatcher and West, *Trans. Roy. Soc.*, 21, 269 (1927).

[3] Benrath and Ruland, *Z. anorg. allgem. Chem.*, 114, 267 (1920).

sulfate and a large excess of formic acid, if kept at 100° for a day, showed no change in the ceric ion content, as determined colorimetrically.

The present authors have studied the oxidation of oxalic acid with ceric sulfate[4] and have based an accurate method for the standardization of ceric sulfate solutions on this reaction.

It seemed probable that ceric sulfate, if its action on formic acid was negligible, could be used with much greater accuracy and under a much wider range of experimental conditions, than could permanganate or other oxidizing agents to determine such acids as tartaric, malic, malonic, etc. In the experimental work which follows such is shown to be the case. Obviously quantitative data can be given for only a few representative acids but the cases listed below will serve to illustrate the possibilities of ceric sulfate as a volumetric oxidizing agent in the determination of organic acids.

Experimental

The ceric sulfate solution was prepared by the method described by the authors[5] from high-grade ceric oxide and was 0.5 M in sulfuric acid. It was standardized against sodium oxalate.[4] The ferrous sulfate solution was standardized electrometrically against standard ceric sulfate.[4] A silver chloride–platinum electrode system was used and a thermionic voltmeter, Type DP-2, from the General Electric Company.

Formic Acid, HCOOH.—In five experiments 15–50 cc. of very pure formic acid 0.1 N as a reducing agent was taken, then 20–60 cc. of sulfuric acid, sp. gr. 1.5, and 25 cc. of 0.1 N ceric sulfate. After diluting to 200 cc. the solution was held just below the boiling point for thirty or sixty minutes. The volume of ceric sulfate used varied from 0.03 cc. at the shorter time and low acidity to 0.21 cc. at the longer time and highest acidity. The average error of 0.12 cc. would correspond to 0.28 mg. of formic acid. Thus formic acid is not appreciably oxidized in hot acid solution by ceric sulfate, a result scarcely to be expected when one considers the ease with which it is oxidized by many oxidizing agents. Its presence as an oxidation product from other organic acids should cause no interference in oxidations with ceric sulfate.

Corrections of 0.03–0.05 cc. have been applied to the above figures, for it was found that in blank experiments in which formic acid was omitted the oxidizing power of ceric sulfate decreased to this extent. In previous experiments[5] using a reflux condenser no change whatever was observed, but in this work a beaker was used.

Acetic Acid, CH_3COOH.—Acetic acid distilled from chromic acid was diluted to a 0.1 *N* acid solution. Two 50-cc. samples of this, after dilu-

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[4] Willard and Young, THIS JOURNAL, 50, 1322 (1928); see also Furman, *ibid.*, 50, 755 (1928).

[5] Willard and Young, *ibid.*, 51, 149 (1929).

tion with 20 cc. of sulfuric acid, sp. gr. 1.5, 25 cc. of ceric sulfate, 0.1020 N, and water to 200 cc., were heated to boiling and held just below the boiling point over a free flame for thirty and sixty minutes, respectively. After cooling and determining the excess ceric salt in the usual way, it was found that 0.05 cc. and 0.10 cc. of the ceric sulfate had been used up in the two experiments. Therefore, acetic acid is not oxidized in hot solution by ceric sulfate.

Tartaric Acid, HOOCCH(OH)CH(OH)COOH.—Mestrezat[6] added a slight excess of permanganate to a hot sulfuric acid solution containing tartaric acid, then an excess of standard oxalic acid, and determined the excess of the latter by back titration with standard permanganate. He gave as the reaction

$$H_2C_4H_4O_6 + 3O = 2HCOOH + 2CO_2 + H_2O \qquad (1)$$

but obtained in this method an oxygen equivalent of 6.86 instead of 6, due to slow oxidation of formic acid. To avoid this error he attempted the complete oxidation of tartaric acid, first in acid, then in alkaline medium, to carbon dioxide and water.

$$H_2C_4H_4O_6 + 5O = 4CO_2 + 3H_2O \qquad (2)$$

and obtained an oxygen equivalent of 9.80 instead of 10. A number of other oxidation methods for tartaric acid have been described.[7]

Benrath and Ruland[3] stated that the velocity of the reaction of tartaric acid with excess ceric sulfate was retarded by the presence of sulfuric acid (their work was carried out at 0 and 20°). This was, therefore, the first matter to be investigated.

Very pure potassium acid tartrate was recrystallized from water, dried at 100° for a short time and used to prepare a standard solution. The tartrate, checked further by titrating three 1-g. samples of it with 0.1 N sodium hydroxide which had been standardized against Bureau of Standards potassium acid phthalate, was found to be 99.91% pure.

Twenty-five cc. portions of potassium acid tartrate solution containing 0.06916 g. of $KHC_4H_4O_6$ or 0.05439 g. of $H_2C_4H_4O_6$ were diluted with water, sulfuric acid, sp. gr. 1.5 and 40 cc. of 0.1020 N ceric sulfate to 200 cc., heated to 90–95° and kept at this temperature on a low temperature hotplate for thirty minutes. The solutions were cooled to 30–35° and the excess ceric sulfate titrated electrometrically with standard ferrous sulfate.

With all factors but the acid concentration at time of oxidation held constant, the extent of oxidation of tartaric acid decreased at first and

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[6] Mestrezat, *Ann. chim. anal.*, 12, 173 (1907); also Chapman and Whitteridge, *Analyst*, 32, 163 (1907); Kling and Florentin, *Bull. soc. chim.*, 11, 886 (1912); Meigen and Schnerb, *Z. angew. Chem.*, 37, 208 (1924).

[7] For example—iodimetric, Strebinger and Wolfram, *Oesterr. Chem.-Ztg.*, 26, 156 (1923); Cuny, *J. pharm. chim.*, [8] 3, 112 (1926); Pirrone, *Riv. ital. essenze e profumi*, 101 (1928)—dichromate, Taufel and Wagner, *Z. anal. Chem.*, 67, 16 (1925).

then increased to a constant value as the acid concentration was steadily increased. In the last four experiments in which the volume of sulfuric acid added varied from 30 to 60 cc., there was a deviation of 0.19 cc. of 0.1020 *N* ceric sulfate, which corresponds to 0.4 mg. of tartaric acid. In the following experiments, therefore, these conditions were used.

Measured volumes of a standard potassium acid tartrate solution (25 cc. = 0.06678 g. of $KHC_4H_4O_6$ or 0.05326 g. of $H_2C_4H_4O_6$) were taken, diluted with water, acid and 0.1020 N ceric sulfate to the volume indicated in Table I, and treated in the same way as the solutions for the experiments described above. The results obtained are shown in Table I.

TABLE I

THE OXIDATION OF TARTARIC ACID WITH CERIC SULFATE IN ACID SOLUTION

H_2SO_4 sp. gr. 1.5, before ox, cc.	Time of standing at 90–95°, min.	Vol. during ox., cc.	0.1020 *N* $Ce(SO_4)_2$ added, cc.	0.1 *N* $Ce(SO_4)_2$ used, cc.	$H_2C_4H_4O_6$ taken, g.	$H_2C_4H_4O_6$ found, g.
30	30	200	40	25.54	0.0533	0.0532
30	60	200	40	25.55	.0533	.0533
30	30	200	30	25.49	.0533	.0531
30	60	200	60	25.55	.0533	.0533
30	10	200	40	25.54	.0533	.0532
30	30	200	100	76.91	.1598	.1603
30	30	200	40	10.21	.0213	.0213
15	30	100	40	25.47	.0533	.0531
45	30	300	40	25.63	.0533	.0534

The amount of tartaric acid oxidized by 1 cc. of 0.1 N ceric sulfate is 0.002084 g. When this factor is used the values in the last column are obtained, the results agreeing very closely with those in the preceding column. Three other series of experiments similar to those in Table I were carried out, in which the sulfuric acid, sp. gr. 1.5, added before oxidation amounted in turn to 40, 50 and 60 cc. per 200 cc. of solution, and the results obtained were of the same degree of accuracy as those above. Thus it is seen that the amount of tartaric acid oxidized by 1 cc. of 0.1 N ceric sulfate remains constant over wide variations in acid concentration, excess of oxidizing agent and time of its action, volume of solution in which the oxidation is carried out and tartaric acid content. According to Table I, 1 mole of tartaric acid requires 7.2 equivalents of oxygen for oxidation; that is, the oxidation reaction, under the conditions used above, cannot be expressed by Equation 1.[8]

Succinic Acid, $HOOCCH_2CH_2COOH$.—Very pure succinic acid which had been recrystallized twice from nitric acid and once from water was used to prepare a 0.05 M solution. Twenty-five cc. portions of this so-

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[8] After this paper had been submitted for publication, Berry [Analyst, 54, 46 (1929)] published some work in which he obtained an oxygen equivalent of 7.02 by the use of ceric sulfate, apparently by direct titration, a reaction too slow to be practicable.

lution were diluted with water, acid and 25 cc. of 0.1020 N ceric sulfate to 200 cc., and treated in the same way as the solutions for the experiments in Table I. The volume of ceric sulfate used varied from 0.06 cc. in half an hour to 0.17 cc. in two hours, indicating that succinic acid is not appreciably oxidized under these conditions.

Malonic Acid, $HOOCCH_2COOH$.—Malonic acid has been titrated directly in hot acid solution with permanganate,[9] the reaction being

$$H_2C_3H_2O_4 + 3O = H_2O + HCOOH + 2CO_2 \tag{3}$$

Later investigators[10] found the method very irregular, due to appreciable oxidation of formic acid, and developed an accurate procedure for malonic acid, based on its complete oxidation, first in acid, then in alkaline medium

$$H_2C_3H_2O_4 + 4O = 2H_2O + 3CO_2 \tag{4}$$

Pure malonic acid was recrystallized from ether and the first fraction of crystals used to prepare a standard solution. Titrations of three samples of this material with 0.1 N sodium hydroxide indicated a purity of 99.59%. Measured volumes of a standard solution (25 cc. = 0.04337 g. of $H_2C_3H_2O_4$) were diluted with water, 0.1020 N ceric sulfate and acid to the volume indicated in Table II, and treated in the same way as the solutions for the experiments with tartaric acid. With malonic acid it was important to add the ceric sulfate before the acid; otherwise, a slight error was introduced, due possibly to decomposition of the malonic acid by the sulfuric acid. The results obtained are shown in Table II.

TABLE II

THE OXIDATION OF MALONIC ACID WITH CERIC SULFATE IN ACID SOLUTION

Bxpt.	H_2SO_4, sp. gr. 1.5, before ox., cc.	Time of standing at 90–95°, min.	Vol. during ox., cc.	0.1020 N $Ce(SO_4)_2$ added, cc.	0.1 N $Ce(SO_4)_2$ used, cc.	$H_2C_3H_2O_4$ taken, g.	$H_2C_3H_2O_4$ found, g.
1	20	30	200	50	27.17	0.0434	0.0425
2	30	30	200	50	27.47	.0434	.0429
3	40	30	200	50	27.72	.0434	.0433
4	50	30	200	50	27.74	.0434	.0434
5	60	30	200	50	27.87	.0434	.0436
6	40	60	200	50	27.73	.0434	.0433
7	60	60	200	50	27.73	.0434	.0433
8	40	30	200	75	27.72	.0434	.0433
9	60	30	200	75	27.86	.0434	.0435
10	40	15	200	50	27.54	.0434	.0430
11	60	15	200	50	27.83	.0434	.0435
12	80	30	400	100	65.22	.0867	.0863
13	20	30	80	35	10.78	.0173	.0169
14	20	30	100	35	10.71	.0173	.0168
15	40	30	200	65	39.23	.0607	.0613
16	40	30	200	65	44.97	.0694	.0703
17	40	30	200	75	56.55	.0867	.0884

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[9] Durand, *Ann. chim.* anal., 8, 330 (1903).

[10] Cameron and McEwan, *Proc.* Chem. *Soc.*, 26, 144 (1910).

Thus, an average of 0.001563 g. of malonic acid is oxidized by 1 cc. of 0.1 *N* ceric sulfate. By the use of this factor the values in the last column are obtained. Experiments 1 to 5 show that the extent of oxidation of a given amount of malonic acid is constant in a solution containing 40–60 cc. of sulfuric acid, sp. gr. 1.5, per 200 cc.; Expts. 3 to 13 show that the results are accurate for a given concentration of malonic acid over wide variations in acid concentration, excess of oxidizing agent and time of its action, and volume of solution in which the oxidation is carried out; Expts. 14 to 17 show that the results become less accurate as the concentration of malonic acid is changed. Because of this effect, the approximate strength of the solution, if unknown, should be determined by a preliminary experiment, that volume which will contain 40–50 mg. of malonic acid taken for the final analyses and the oxidation carried out in a volume of 200 cc. These experiments show that 1 mole of malonic acid requires 6.66 equivalents of oxygen for oxidation.

Glycolic Acid, $CH_2(OH)COOH$.—The acid was purified by recrystallizing from ether, and the first fraction of crystals used to prepare a standard solution. Titrations of three samples of acid with 0.1 N sodium hydroxide indicated *a* purity of 99.75%. Preliminary experiments showed that glycolic acid was not as easily oxidized by ceric sulfate as tartaric or malonic acid, a steady increase in oxidation being evident over a five-hour period with solutions kept at 90–95°. Therefore, measured portions of the standard solution (25 cc. = 0.05131 g. of $HC_2H_3O_3$) were diluted with water, 0.1020 *N* ceric sulfate and acid to the volume indicated in Table III, heated to boiling, held just below the boiling point over a small flame for the time indicated, then cooled to 30–35° and titrated electrometrically with standard ferrous sulfate. The results are shown in Table III.

TABLE III

THE OXIDATION OF GLYCOLIC ACID WITH CERIC SULFATE IN ACID SOLUTIONS

Expt.	H_2SO_4, sp. gr. 1.5, before ox., cc.	Time at b. p., min.	Vol. during ox., cc.	0.1020 N $Ce(SO_4)_2$ added, cc.	0.1 N $Ce(SO_4)_2$ used, cc.	$HC_2H_3O_3$ taken, g.	$HC_2H_3O_3$ found, g.
1	40	30	200	50	25.80	0.0513	0.0496
2	40	60	200	50	26.60	.0513	.0512
3	40	120	200	50	26.78	.0513	.0515
4	60	60	200	50	26.62	.0513	.0512
5	60	120	200	50	26.52	.0513	.0510
6	40	60	200	50	10.75	.0205	.0207
7	40	60	200	75	53.18	.1026	.1023
8	20	60	100	50	26.76	.0513	.0515
9	60	60	300	50	25.13	.0513	.0483
10	60	60	300	75	26.95	.0513	.0518
11	40	60	200	75	26.93	.0513	.0518
12	60	60	200	75	26.75	.0513	.0515

The amount of glycolic acid oxidized by 1 cc. of 0.1 N ceric sulfate, according to these experiments, is 0.001923 *g.* Experiment 1 shows that the extent of oxidation of glycolic acid is not constant after contact with excess ceric sulfate for thirty minutes in hot solution and Expt. 9 that the excess of ceric sulfate used there is not sufficient for the larger volume of solution. The other experiments indicate that an accurate determination of glycolic acid may be made within a wide range of conditions. According to Table VI 1 mole of glycolic acid requires 3.95 equivalents of oxygen for oxidation, that is, the reaction may be

$$HC_2H_3O_3 + 2O = HCOOH + CO_2 + H2O \qquad (5)$$

Malic **Acid,** $HOOCCH_2CH(OH)COOH$.—Mestrezat[6] used procedures for malic acid similar to those developed for tartaric acid. By oxidation with permanganate in acid solution

$$H_2C_4H_4O_5 + 4O = 2HCOOH + 2CO_2 + H_2O \qquad (6)$$

he obtained an oxygen equivalent of 8.81 instead of 8, and by oxidation first in acid, and finally in alkaline solution

$$H_2C_4H_4O_5 + 6O = 4CO_2 + 3H_2O \qquad (7)$$

his oxygen equivalent was 11.40 instead of 12. Lange and Kline[11] did not obtain satisfactory results in titrating malic acid in hot solution with permanganate.

Malic acid was purified by dissolving in hot acetone, filtering and adding carbon tetrachloride to the hot solution and allowing the acid to crystallize on cooling. Three samples, dried at 100–110°, indicated a purity of 99.59% when titrated against 0.1 N sodium hydroxide. The treatment of measured portions of a standard solution of malic acid was similar to that described for the experiments in Table III. The volume at the time of oxidation was always 200 *cc.* Results obtained are given in Table IV.

Thus, 0.001449 g. of malic acid is oxidized by 1 cc. of 0.1 N ceric sulfate. Using this factor, the values in the last column are obtained. Experiments 1 to 5 show that the extent of oxidation of malic acid is constant in a solution containing 40–60 cc. of sulfuric acid, sp. gr. 1.5, per 200 cc.; Expts. 4 to 13 show that the results are accurate for a given concentration of malic acid over wide variations in acid concentration, excess of oxidizing agent and time of its action; Expts. 14 to 16 show that the results become less accurate as the concentration of malic acid is changed. With variations in the volume the results were not satisfactory. Therefore, it is necessary to determine the approximate concentration of the solution and to use a volume which will contain 40–60 mg. of malic acid, carrying out the oxidation in a volume of 200 cc. In these experiments 1 mole of malic acid requires 9.25 equivalents of oxygen for oxidation.

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[11] Lange and Kline, THIS JOURNAL, 44, 2709 (1922).

TABLE IV

THE OXIDATION OF MALIC ACID WITH CERIC SULFATE IN ACID SOLUTION

Expt.	H_2SO_4, sp. gr 1.5, before ox, cc.	Time at b. p., min.	0.1020 N $Ce(SO_4)_2$ added, cc.	0.1 *N* $Ce(SO_4)_2$ used, cc.	$H_2C_4H_4O_5$ taken, g.	$H_2C_4H_4O_5$ found, g.
1	20	30	50	28.69	0.0423	0.0416
2	30	30	50	28.64	.0423	.0415
3	40	30	50	28.88	.0423	.0419
4	50	30	50	29.07	.0423	.0421
5	60	30	50	29.21	.0423	.0423
6	40	60	50	29.09	.0423	.0422
7	60	60	50	29.07	.0423	.0421
8	40	120	50	29.09	.0423	.0422
9	60	120	50	29.35	.0423	.0425
10	40	15	50	28.89	.0423	.0419
11	60	15	50	29.13	.0423	.0422
12	40	30	75	29.05	.0423	.0421
13	60	30	75	29.34	.0423	.0425
14	40	30	50	22.72	.0338	.0329
15	40	30	75	35.26	.0507	.0511
16	40	30	75	41.11	.0593	.0596

Citric Acid, $HOOCCH_2C(OH)COOHCH_2COOH$.—From a study of the oxidation of citric acid by permanganate, Wöhlk[12] found that these substances reacted with each other, with or without the addition of mineral acid. In a direct titration with permanganate in hot dilute sulfuric acid solution, he considered that acetone-dicarboxylic acid, a primary oxidation product, split up quickly into acetone and carbon dioxide, these being the chief products of the oxidation. In a secondary oxidation reaction, the acetone was further split up to some extent into acetic and formic acids.

$$H_3C_6H_5O_7 + O = C_3H_6O + 3CO_2 + H_2O \qquad (8)$$

$$C_3H_6O + 3O = HC_2H_3O_2 + HCOOH \qquad (9)$$

Pratt's method[13] for citric acid, depending upon its fractional oxidation by permanganate to acetone, removal of the acetone as fast as formed by distillation, formation of an insoluble mercury–acetone complex and the weighing of this precipitate, has been modified by Willaman[14] to give more satisfactory results. Cuny[7] has described an iodimetric method for citric acid, complete oxidation to carbon dioxide being effected.

$$5H_3C_6H_5O_7\cdot H_2O + 9I_2O_5 = 9I_2 + 30CO_2 + 25H_2O \qquad (10)$$

A solution of citric acid was prepared from pure material and standardized by titrating three 100-cc. samples with 0.1 N sodium hydroxide. The treatment of measured portions of this standard acid solution (25

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[12] Wohlk, Z. *anal. Chem.*, *41*, 77 (1902); see also Mathieu and Ferre, *Ann. chim. anal.*, 18, 352 (1913).

[13] Pratt, U. S. Dept. Agr., Bur. Chem., *Cir.* 88.

[14] Willaman, THIS JOURNAL, 38, 2193 (1916).

cc. = 0.04995 g. of $H_3C_6H_5O_7$) was similar to that described for the experiments in Table III. Results obtained are given in Table V.

TABLE V

THE OXIDATION OF CITRIC ACID WITH CERIC SULFATE IN ACID SOLUTION

Expt.	H_2SO_4, sp. gr. 1.5, before ox., cc.	Time at b. p., min.	Vol. during ox., cc.	0.1020 *N* $Ce(SO_4)_2$ added, cc.	0.1 *N* $Ce(SO_4)_2$ used, cc.	$H_3C_6H_5O_7$ taken, g.	$H_3C_6H_5O_7$ found, g
1	20	30	200	75	40.75	0.0500	0.0494
2	30	30	200	75	41.29	.0500	.0500
3	40	30	200	75	41.14	.0500	.0498
4	50	30	200	75	41.22	.0500	.0499
5	60	30	200	75	41.29	.0500	.0500
6	30	30	200	100	41.25	.0500	.0500
7	50	30	200	100	41.71	.0500	.0505
8	30	30	200	60	40.92	.0500	.0496
9	50	30	200	60	41.04	.0500	.0497
10	30	60	200	60	41.11	.0500	.0498
11	50	60	200	60	41.30	.0500	.0500
12	50	30	200	60	32.72	.0400	.0396
13	50	30	200	75	50.18	.0600	.0608
14	50	30	200	75	58.31	.0700	.0706
15	25	30	110	60	42.38	.0500	.0513
16	75	30	300	75	40.59	.0500	.0492

Thus, 0.001211 g. of citric acid is oxidized by 1 cc. of 0.1 N ceric sulfate. Experiment 1 indicates that there was not enough sulfuric acid added. The results are somewhat less accurate in Expts. 12 to 14, as the citric acid content is changed and in Expts. 15–16 the volume is changed. The other experiments indicate that an accurate determination of citric acid may be made within a wide range of conditions. To use the conversion factor given above, the approximate strength of the solution if unknown should be determined by a preliminary experiment, that volume which will contain 40–60 mg. of citric acid taken for the final analyses, and the oxidation carried out in a volume of 200 cc. According to Table V, 1 mole of citric acid requires 15.85 equivalents of oxygen for oxidation, an indication that the oxidation of the acetone is very extensive.

Maleic and Fumaric Acids, HOOCCH=CHCOOH.—Lange and Kline[11] stated that maleic or fumaric acid could be titrated with permanganate in hot acid solution and assumed that the reaction was

$$H_2C_4H_2O_4 + 5O = 3CO_2 + HCOOH + H_2O \qquad (11)$$

Their results were not altogether satisfactory and they did not recommend the method. Sabalitschka and Tietz[15] reported that accurate results could be obtained if excess permanganate was added to the hot acid solution, followed by oxalate, and the excess of the latter determined by titration with permanganate. They gave as the reaction

$$H_2C_4H_2O_4 + 30O = 20CO_2 + 10H_2O \qquad (12)$$

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[15] Sabalitschka and Tietz, *Continental Met. and Chem. Eng.*, 2, 232 (1927).

It was thought that both of these acids would be easily oxidized by ceric sulfate, but such did not prove to be the case. Several 31-mg. samples of each acid, in volumes of 200 cc. containing 20–60 cc. of sulfuric acid, sp. gr. 1.5, and 50 cc. of 0.1020 N ceric sulfate, reacted at 95° with 0.68–0.98 cc. (fumaric acid) or 0.35–0.61 cc. (maleic acid) of 0.1 *N* ceric sulfate in a half hour. In an hour with a 62-mg. sample of either acid, less than 2 cc. of 0.1 *N* ceric sulfate was used.

Benzoic Acid, C_6H_5COOH.—Benzoic acid, though resistant in general to oxidizing agents, was oxidized to a considerable extent by ceric sulfate. For example, a 0.0987-g. sample of the acid was dissolved, diluted with water, 60 cc. of sulfuric acid, sp. gr. 1.5, and 50 cc. of 0.1020 *N* ceric sulfate to 200 cc., heated to boiling and kept just below the boiling point for two hours. After cooling the solution and determining the excess ceric sulfate in the usual way, it was found that 29.10 cc. of 0.1 *N* ceric sulfate had been used for oxidation. Another sample of the same weight was dissolved, diluted with 40 cc. of sulfuric acid, sp. gr. 1.5, and 100 cc. of 0.1020 N ceric sulfate to 200 cc., and held just below the boiling point for three hours. In this case 39.63 cc. of 0.1 N ceric sulfate was used for oxidation. Other experiments covering a wide range of conditions indicated that the extent of oxidation of benzoic acid was not definite.

Phthalic **Acid,** *o*-$C_6H_4(COOH)_2$.—Several 43-mg. samples of phthalic acid, in volumes of 200 cc. containing 30–50 cc. of sulfuric acid, sp. gr. 1.5, and 25 cc. of 0.1020 *N* ceric sulfate, reacted at 95° with only 1.49–1.98 cc. of 0.1 *N* ceric sulfate in a period of one hour. The oxidation of phthalic acid by ceric sulfate was, therefore, very slight.

Salicylic **Acid,** $C_6H_4(OH)COOH$.—Several 19-mg. samples of salicylic acid, in volumes of 200 cc. containing 20–60 cc. of sulfuric acid, sp. gr. 1.5, and 50 cc. of 0.1020 *N* ceric sulfate, reacted at 95° with 28.50–32.18 cc. of 0.1 N ceric sulfate over periods of one-half to two hours. The oxidation of salicylic acid was very extensive but not constant.

Discussion

These results prove that the oxidizing action of ceric sulfate on organic materials may be very different from that of potassium permanganate or chromic acid. For this reason ceric sulfate may be of use in certain organic oxidations where permanganate or chromic acid either do not act or do not bring about the reaction desired—possibly, for example, in some oxidations to determine structure. The fact that formic acid, which is an aldehyde as well as an acid, is not oxidized by ceric salt but is slowly attacked by permanganate suggests the possibility of oxidizing alcohols quantitatively to aldehydes with ceric salt. The authors intend to investigate this matter as well as the action of ceric sulfate on other types of organic compounds. Preliminary experiments indicate that some organic substances can be oxidized by direct titration with ceric sulfate.

Though none of the acids listed above can compare in accuracy with oxalic acid (used as sodium oxalate) as primary standards in oxidimetry reactions, a number of them have been suggested as primary standards in acidimetry reactions, notably maleic, fumaric, malic and tartaric in the form of potassium acid tartrate. The authors found potassium acid tartrate to be by far the most satisfactory of these four. It is obtained in very pure form by one recrystallization, and compares favorably in accuracy with potassium acid phthalate, an accepted primary standard in acidimetry.

Summary

1. Formic, acetic, succinic, fumaric and maleic acids are not oxidized by ceric sulfate in hot sulfuric acid solution.

2. Tartaric, malonic, malic, glycolic and citric acids are oxidized under the same conditions, the products being, usually, formic acid and carbon dioxide. Because the formic acid is not oxidized by ceric sulfate, it has been possible to develop accurate analytical procedures for each of this last group of acids, based on their oxidation in hot sulfuric acid solution by excess standard ceric sulfate and titration of the excess with standard ferrous sulfate.

3. Benzoic, phthalic and salicylic acids are oxidized to a variable extent by ceric sulfate in hot sulfuric acid solution.

4. Attention is called to the possibility of using ceric sulfate in certain organic oxidations where the usual reagents, such as permanganate or dichromate, either do not act or do not produce the result desired.

ANN ARBOR, MICHIGAN

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

PYROPHORIC IRON. I. PREPARATION AND PROPERTIES[1]

BY T. G. FINZEL

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The pyrophoric property of properly prepared finely divided iron reacting with air at room temperatures is a well-known phenomenon.[2] It has been definitely established, moreover, that such material becomes non-pyrophoric when subjected to a high temperature.

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[1] The subject of this research was suggested by Professor James H. Walton and the investigation was conducted under his direction. (Manuscript first received August 30, 1928.)

[2] Magnus, *Pogg. Ann.*, 3, 81 (1825); Moissan, *Ann. chim. phys.*, [5] *21*, 199–256 (1880); Birnie, *Rec. trao. chim.*, *2*, 273–294 (1883); Smits, Kettner and de Gee, *Verslag. Akad. Wetenschappen*, Amsterdam, [II] *16*, 999 (1913); Tammann and Nikitin, *Z. anorg. allgem. Chem.*, *135*, 201–204 (1924).

Pyrophoric iron has been prepared in many ways, among which may be enumerated the thermal decomposition of ferrous oxalate, reduction of ferrous oxalate by hydrogen, reduction of ferric oxide or a mixture of ferric oxide and aluminum oxide by either hydrogen or carbon monoxide and the reduction of ferrous oxide or carbonate by hydrogen. In most cases definite conditions for the preparation of the pyrophoric materials are not mentioned in the literature nor are the pyrophoric products properly identified. Consequently the term pyrophoric iron includes any pyrophoric ferrous material containing any amount of metallic iron. The references on the preparation of pyrophoric iron indicate that such factors as temperature, length of time of heating or reduction and the condition of the starting material are exceedingly important in obtaining concordant results. To explain pyrophoric action and the inactivation of pyrophoric materials, several theories have been proposed, among which may be named Magnus'[2] theory of fineness of division; that of Moissan,[2] who believed that, in general, so-called pyrophoric iron owes its pyrophoric activity to finely divided FeO; the metastable equilibrium theory of Smits;[2] and the surface theory of Tammann and Nikitin.[2]

According to Hofmann,[3] the smaller the oxide particle, the greater will be the rate and the extent of reduction, and the greater will be the tendency for the iron particles to adhere to each other so as to diminish the surface. If pyrophoric activity is dependent upon the extent of the surface of the individual particles, the degree of dispersion of the iron oxide from which the pyrophoric iron is to be prepared should have an effect on the pyrophoric activity and also on the inactivation of the resulting iron.

To prepare the true metallic pyrophoric iron in the highest state of purity, it is advisable to avoid all organic compounds. Oxalates or carbonates upon heating or reduction tend to form finely divided carbon. Even carbon dioxide will react with finely divided iron at 500° as shown by Herschkowitsch,[4]

The present paper deals chiefly with the preparation of pyrophoric iron with the highest possible metallic iron content, the effect of the condition of the starting material and the effect of various gases on the inactivation of pyrophoric iron.

Experimental

Ferric oxide precipitated from a ferric nitrate solution by ammonia was used as a starting material in this work. Ferric nitrate was chosen in preference to ferric chloride as it was found that chlorides inhibit the formation of pyrophoric iron while the oxides of nitrogen apparently do not. It has been shown by von Weimarn[5] that if substances

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[3] Hofmann, *Z. angew. Chem.*, **38,** *715–721* (1925).

[4] Herschkowitsch, *Z. anorg. allgem. Chem.*, 115, *159* (1921)

[5] Von Weimarn, *Chem. Rev.*, 2, 228 (1925).

are precipitated from solutions of different concentrations, a difference in the degree of dispersion of the precipitate will result. Thus, in two samples of ferric oxide, the degree of dispersion should be greater in the one precipitated from the more concentrated solution of ferric nitrate. Ferric oxide as a colloidal sol would also be in a state of high dispersion. With this principle in mind, the ferric oxide used in this work was prepared in three ways. *Ferric oxide A* was prepared by precipitation from a hot ferric nitrate solution containing 100 g. of $Fe(NO_3)_3 \cdot 9H_2O$ per liter of water, using an excess of NH_4OH (sp. gr. 0.90). The oxide was freed from salts and ammonia by decantation and washing, dried at 110–120° and ground to a fine powder in an agate mortar. *Ferric oxide* B was prepared in a manner similar to the preparation of oxide A with the exception that the concentration of the ferric nitrate solution was 25 g. per liter. *Ferric oxide C* was obtained by hydrolysis of 10 g. of ferric nitrate per liter of boiling water, so as to produce a colloidal sol. It was subsequently dialyzed in collodion bags at 90–95° for approximately one week, after which time the sol was almost free from the nitrate ion. This method for preparation of the sol is similar to that described by Sorum.[6] The sol was slowly evaporated to dryness in an electric oven held at about 140". Oxides A-11, B-II, etc., represent different samples of the oxides prepared in the same manner as A and B, respectively.

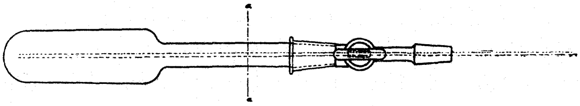

Fig. 1.—Reduction tube.

Preparation of Pyrophoric Iron.—The pyrophoric iron was prepared by hydrogen reduction of approximately two grams of iron oxide placed either in a drawn-out test-tube or in a container similar to that shown in Fig. 1. The latter consisted of a tube fitted with a stopcock and ground-glass joints which permitted it to be attached to a high vacuum apparatus for subsequent degassing of the iron. The hydrogen, previously carefully purified by passage through hot copper, soda lime and phosphorus pentoxide, was passed into the tube through a small capillary. In each case reduction was continued for three hours at 500°, using a gas flow of approximately 80 cc. per minute.

Inactivation of Pyrophoric Iron by Heating in Hydrogen, Nitrogen or Helium.—It is known that pyrophoric iron becomes inactive when heated ior an extended length of time. Consequently, experiments were carried out to determine the effect of the following factors upon the pyrophoric property of iron: the length of time of heating, the method of preparation of the oxide from which the iron was reduced and the gaseous medium in which the pyrophoric iron was heated. Samples of pyrophoric iron prepared in drawn-out test-tubes as described above were placed in a furnace held at 600° for various lengths of time, after which the tubes were removed from the furnace and allowed to cool, hydrogen passing through the capsules continually. When cool, the contents of the tubes were thrown into the air and their pyrophoric or non-pyrophoric property noted.

In preparing the samples of iron to be heated in nitrogen or helium, all samples were reduced in the manner described above. After reduction, these samples were degassed at 500° for approximately one hour until the pressure dropped to at least 5×10^{-5} mm. of mercury. The

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[6] Sorum, THIS JOURNAL, 50, 1263 (1928).

bulb was then filled with dry oxygen-free nitrogen or helium at approximately atmospheric pressure and heated for various lengths of time as indicated in Table I.

TABLE I

EFFECT OF HEATING PYROPHORIC IRON IN HYDROGEN, NITROGEN OR HELIUM

Oxide sample	Condition	Time of heating, hours			
		H_2 (600°)	N_2(600°)	He (600°)	He (625°)
A	Pyrophoric	1.5	6	70	..
	Non-pyrophoric	2.5–3	..	156	42
A-I1	Pyro.	1	5–9	144	..
	Non-pyro.	3	11	...	..
B	Pyro.	12.5	45	...	..
	Non-pyro.	17	..	...	..
13-11	Pyro.	....	..	73.5	..
	Non-pyro.	....	..	160	..
B-III	Pyro.	....	..	...	48.5
	Non-pyro.	....	..	...	..
C	Non-pyro.	1	1	1	1

In every case the pyrophoric iron was black while the non-pyrophoric form was gray-black or decidedly gray From the results obtained by heating in nitrogen and hydrogen, it is evident that iron C loses its pyrophoric property the most rapidly, A and B following next in order. The time for inactivation was greater for heating in nitrogen or helium than in pure hydrogen. Helium required the greatest length of time.

The difference between Samples A, B and C is one of preparation or, as previously pointed out, one of dispersion. It thus appears that the oxide of the lowest degree of dispersion yields pyrophoric iron which is the most difficult to inactivate. As previously mentioned, Hofmann[3] found that the smaller the oxide particles the greater will be the extent of reduction and the greater will be the tendency for the iron covered oxide particles to adhere to each other so as to diminish the total surface. It thus appears that inactivation of pyrophoric iron consists in a decrease of the total surface. This is also in accord with Tammann's views. From Table I, it can also be seen that iron from any particular oxide sample can be more easily inactivated in hydrogen than in nitrogen or helium, the latter taking the longest time. One possible explanation for this difference is that at 600° hydrogen and nitrogen are absorbed and combine to form hydrides and nitrides with the active iron, thus causing it to become inactive, while helium is non-reactive with the iron and consequently allows it to remain pyrophoric for a greater length of time. However, it is known that iron reduced at 500° contains an abundance of absorbed hydrogen and is still pyrophoric; also, iron heated at **500** or 600° gives the a-iron x-ray diagram with no indication of swelling of crystal lattice or evidence for any new lines. Inasmuch as oxide B has the lowest degree of dispersion on the basis of von Weimarn's theory and is also the most difficult to inactivate, it might seem probable that the pyrophoric iron particle contains a small core of oxide which hinders recrystallization of the iron. Heating in hydrogen at a temperature higher than its reduction temperature (500") should then cause further reduction and also facilitate the removal of the water vapor thus formed so as to increase coalescence of the iron atoms. The larger the oxide particle, the larger the residual oxide core and consequently the longer will be the time necessary for inactivation. On this basis, however, it seems impossible to explain the large difference found in the inactivation in nitrogen and helium.

Analysis of the Samples of Iron.—The metallic iron content of the pyrophoric and non-pyrophoric samples of iron was determined by measuring the amount of hydrogen liberated from dilute sulfuric acid solution. Approximately 0.4 g. of iron was prepared by reducing the desired oxide in hydrogen in a small tared capsule, the neck of which was slightly constricted. After reduction, the capillary, through which hydrogen was introduced into the capsule, was withdrawn and the neck of the capsule quickly sealed off while still hot, thus causing a partial vacuum upon cooling. The weight of the iron was obtained as the difference between the gross and tare weights of the capsule. The determination was carried out by breaking the capsule under pure water, which was later acidified with sulfuric acid. The hydrogen liberated was collected and measured in a buret, reduced to standard conditions of temperature and pressure and the metallic iron equivalent calculated. To check the accuracy of the results a determination was made on a sample of pure iron wire the analysis of which was known. The results are given in Table II.

TABLE II

METALLIC IRON CONTENT OF PYROPHORIC AND NON-PYROPHORIC IRON

Oxide reduced	Temp., °C.	Time, hrs.	Yield, %	Condition
B	500	3	98.5	Pyrophoric
B	500	14	98.4	Pyrophoric
B (Constantly agitated)	500	10.5	99.1	Pyrophoric
B	400	24	97.6	Pyrophoric
C	500	12.5	99.0	Pyrophoric
A	625	4	98.5	Non-pyrophoric
Standard iron wire, 99.7% Fe	...	...	99.4	....

From these results it is evident that with the sample used reduction at 500° in hydrogen for three hours is practically the optimum condition for the preparation of pyrophoric iron. It is further shown that there is no essential difference in the iron content of the various samples reduced at 500" and above, whether they be pyrophoric or not.

Microscopic examination of the pyrophoric and non-pyrophoric forms of the most easily inactivated iron, Sample C, was carried out by breaking sealed capsules of both forms of iron under paraffin oil and examining the suspension. The difference in the samples (see Figs. 2 and 3) is in the sizes of the respective clusters or lumps of iron, suggesting that adhesional forces were at play during the heating of the iron. Both photographs are of the same magnification, the distance between the two small lines in Fig. 3 representing 0.1 mm.

Fig. 2.—Pyrophoric iron.

X-Ray examination of pyrophoric iron prepared by reducing oxide C at 400° for twenty-four hours in a special tube (Fig. 4) to prevent entrance of air was carried out as follows: the reduction tube (Fig. 4) was constructed so that it could be sealed off at a-a and b-b after reducing the oxide in the bulb. The active iron was shaken into the capillary, which was then sealed off at c-c. The diffraction lines showed the iron to be of the a-variety with the same pattern as the non-pyrophoric iron which was heated to 650°. Those due to the pyrophoric material appeared slightly more diffused than those shown by iron heated at 650° in hydrogen, indicating a smaller particle size for the pyrophoric iron. Similar results have been obtained by Wyckoff and Crittenden[7] in their studies of ammonia catalysts.

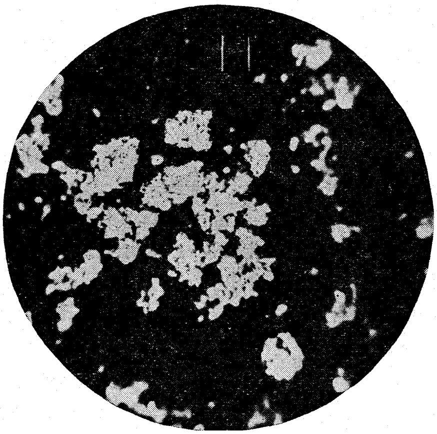

Fig. 3.—Non-pyrophoric iron.

Method for Determining the Degree of **Pyrophoric** Activity.—A measure of the relative pyrophoric activities of the samples of iron was obtained by determining the limiting concentration of oxygen in an oxygen–nitrogen mixture which would just cause pyrophoric action when a sample of the iron was dropped through the gaseous mixture. A gaseous mixture of the desired composition was prepared in a glass tube **30** cm. in length, one end of which was fitted with a rubber stopper through which passed a glass tube. The sealed capsule containing the prepared sample of iron was attached to this glass tube by means of a tough

[7] Wyckoff and Crittenden, THIS JOURNAL, 47, 2866 (1925).

rubber tube which could be squeezed with a pair of pliers, thereby breaking the neck of the capsule and allowing the iron to drop through the gaseous mixture. The observations were made in the dark so that the slightest indications of pyrophoric activity could be noticed. One-gram samples of iron were prepared by hydrogen reduction at 500°, the reduction being carried out until 1.0 mg. or less of water was liberated per hour. As a check on the preparation of the sample, the iron after being dropped through the tube, was thrown into the air. In all cases, the samples which failed to ignite in the prepared oxygen–nitrogen mixture afterward took fire when dropped into the air. The results obtained by this method are given in Table III.

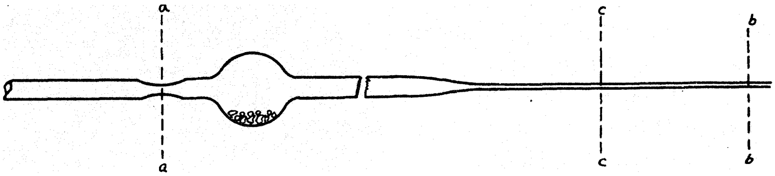

Fig. 4.—Preparation tube for x-ray sample.

TABLE III

LIMITING CONCENTRATION OF OXYGEN IN WHICH PYROPHORIC IRON IS ACTIVE

Oxide sample	A-I1			B			C		
Oxygen concn., %	5	3	5	10	3	1	9.4	5	3
Condition	Pyro.	Non-pyro.	Pyro.	Pyro.	Pyro	Non-pyro.	Pyro.	Non-pyro.	Non-pyro.

From these data, it is evident that the limiting oxygen concentrations for the various samples of iron are as follows: C, between 5 and 9.4%; A, between 3 and 5%; B, between 1 and 3%. This would put the oxides in the order of their increasing pyrophoric activity as C, A, B, an order which is just the reverse of what one would predict from a consideration of a method for preparation of the three oxides. The colloidal oxide, being the most finely divided, should yield the iron having the greatest surface per unit mass, the surface factor, according to Tammann being the criterion for pyrophoric activity. However, referring to the results obtained in heating the pyrophoric iron in hydrogen and also in nitrogen, it will be seen that C became non-pyrophoric in the shortest length of time, A followed and B remained active the longest, probably due to the degree of incompleteness of reduction of the oxides. It is very probable that the inactivation process caused by adhesion or recrystallization is operative at temperatures as low as 500°, the iron containing the most residual oxide remaining pyrophoric the greatest length of time and also being the most pyrophoric when tested by this method. In the following paper it is shown that the adsorptive capacities of the samples of iron for ammonia and carbon dioxide also increase in the order C, A, B.

Reaction of Pyrophoric Iron at −78° and with Dried Air.—A sample of oxide B was reduced in a capsule at 500° in hydrogen for three hours, after which time the neck of the capsule was sealed. The sample was allowed to drop into a glass tube 18 inches long, the sample, tube and air within the tube being cooled to −78° for one-half hour by means of carbon dioxide, snow and ether. A trigger was placed in a side-arm of the 18-inch tube to break the capsule and allow the iron to drop through the cold air. No precautions were taken to prevent the diffusion of the carbon dioxide through the side-arm and into the tube. The iron falling through the tube was exceedingly pyrophoric, heating the air in the tube to such an extent that some of the finely divided iron was blown out of the side-arm.

It was also found that properly prepared iron was pyrophoric when allowed to drop through air dried for two to three months over phosphorus pentoxide. The iron samples were prepared from oxide A, reduced at 500° by hydrogen. The capsules containing the iron were evacuated to 10^{-3} mm. pressure at 500°, filled with nitrogen and sealed.

Summary

1. Pyrophoric iron can best be prepared by reducing precipitated ferric oxide by hydrogen at 500°.
2. Ferric nitrate is a suitable starting material for the preparation of the ferric oxide. Chlorides are to be avoided as they destroy the pyrophoric property of the iron.
3. For pyrophoric iron prepared from a definite sample of oxide, inactivation is dependent not only upon the temperature and time of heating but also upon the gaseous medium in which it is heated.
4. Accepting von Weimarn's precipitation law, the time necessary for inactivation of pyrophoric iron is dependent upon the degree of dispersion of the oxide from which it is reduced.
5. Iron was found to be pyrophoric in dried air and also in air cooled to −78°.
6. A method was devised for the determination of the degree of pyrophoric activity of iron.

MADISON, WISCONSIN

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

PROPERTIES OF PYROPHORIC IRON. II. ADSORPTION OF CARBON DIOXIDE AND AMMONIA AND THE USE OF PYROPHORIC IRON IN THE AMMONIA SYNTHESIS[1]

BY T. G. FINZEL

RECEIVED AUGUST 16, 1929 PUBLISHED JANUARY 8, 1930

In a previous paper,[2] it was shown that the pyrophoric activity of iron prepared by the reduction of ferric oxide in hydrogen was influenced by the method of preparation of the oxide. The greater the degree of dispersion of the ferric oxide, the more easily was pyrophoric iron converted into the non-pyrophoric form when heated to a temperature higher than the reduction temperature.

This investigation is an attempt to find any relationship between the differences in the ease of inactivation of the three samples of pyrophoric iron and their adsorptive and catalytic properties.

Materials for Adsorption

Gases.—Carbon dioxide was prepared by dropping sulfuric acid into a saturated solution of sodium bicarbonate, previously boiled to remove any dissolved air. The gas was dried by concentrated sulfuric acid and phosphorus pentoxide. Pure ammonia was prepared by heating a concentrated solution of ammonium hydroxide, passing the gas through a strongly alkaline solution of pyrogallol and finally over soda lime and flaked caustic soda. Nitrogen, used to determine the free volume of the adsorption bulb, was obtained from a cylinder of the gas. It was passed through concentrated sulfuric acid, over hot copper and finally dried over phosphorus pentoxide. Hydrogen for the reduction of ferric oxide was commercial gas produced by the electrolysis of caustic soda solution. It was purified by passing through concentrated sulfuric acid, soda lime, hot copper, soda lime and phosphorus pentoxide in the order named.

Iron Oxides.—Ferric oxides A and B were precipitated from a ferric nitrate solution by ammonium hydroxide, while ferric oxide C was prepared from a colloidal sol, using ferric nitrate and in one case ferric chloride as a starting material. The preparation of these oxides has been described in Part I.[2]

Preparation of the Iron for Adsorption

The reduction of the iron oxide was carried out in the adsorption bulb, illustrated in Fig. 1 of the previous paper.[2] In all cases pyrophoric iron was prepared by hydrogen reduction at 500°, the hydrogen being passed into the bulb by means of a small capillary tube at a rate approximating 80 cc. per minute. During the reduction the bulb was removed several

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[1] The work in this paper and Part I is from the thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. The subject of this research was suggested by Professor James H. Walton and the investigation was carried out under his direction. (Manuscript first received November **13, 1928.)**

[2] Finzel, THIS JOURNAL, 52, **142 (1930).**

times from the furnace and the material shaken to break up any lumps of material formed during the early stages of the reduction. After about ten hours of reduction a T-tube to which was connected a U-tube containing phosphorus pentoxide was attached to the adsorption bulb. Reduction was stopped when the gain in weight of this U-tube showed that the water liberation had dropped to approximately 0.5 to 1.5 mg. per hour. The iron was degassed at 500° by means of a mercury vapor and oil pump until the pressure dropped to at least 5×10^{-5} mm. pressure. Three to five hours was the usual time for degassing, depending upon the kind of iron in the bulb.

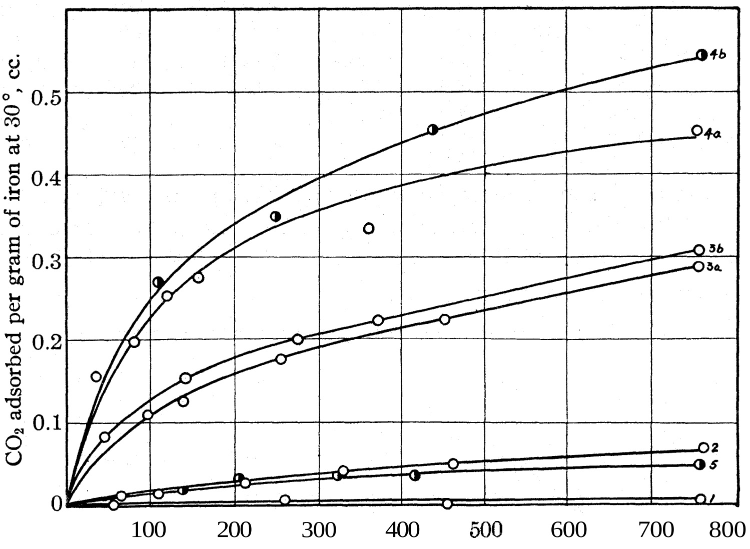

Fig. 1.—Adsorption of carbon dioxide by pyrophoric iron.

Adsorption Results.—The free volume of the adsorption bulb was determined by two methods; in the first the volume of the iron in the bulb was subtracted from the volume of the empty bulb while in the second the volume of nitrogen necessary to fill the bulb containing the iron was determined. Since it was found that the two methods agreed within experimental error, the former was generally used. The adsorptive capacities of the pyrophoric and non-pyrophoric iron samples for carbon dioxide and ammonia at the highest equilibrium pressure and at 30° are given in Table I, the complete isotherms being illustrated graphically in Figs. 1 and 2.

By comparing Curves 2 and 5 (Fig. 1), it is evident that the pyrophoric iron reduced at 500° from oxide C adsorbed less carbon dioxide than the non-pyrophoric iron reduced at 625° from oxide A. It is evident that

TABLE I

ADSORPTION OF CARBON DIOXIDE AND AMMONIA BY PYROPHORIC AND NON-PYROPHORIC IRON AT 30°

Curve	Oxide	Gas	Reduction temp., °C.	Reduction time, hrs.	Pressure, mm.	Cc. ads. per *g.* of iron	Condition
1	A	CO_2	500	11	757.6	0.004	Non-pyro.
			650	2.5			
2	A		625	12	760.9	0.065	Non-pyro.
3a	A		500	12.5	757.7	.292	Pyro.
3b	A		500	11	757.4	.309	Pyro.
4a	B		500	13	754.4	.454	Pyro.
4b	B		500	11	759.0	.545	Pyro.
5	C		500	12	759.7	.046	Pyro.
6	A-III	NH_3	500	23	758.0	.935	Pyro.
7	B-II		500	22.5	266.4	.950	Pyro.
8	C *ex*		500	12	432.7	.397	Pyro.
	$FeCl_3$		500	22			
9	A-III		650	5	754.2	.188	Non-pyro.

adsorption of this particular gas is not a criterion for judging pyrophoric activity. For the pyrophoric samples, adsorption of both carbon dioxide and ammonia increased in the order C, A, B, the last showing the largest adsorption in each case.

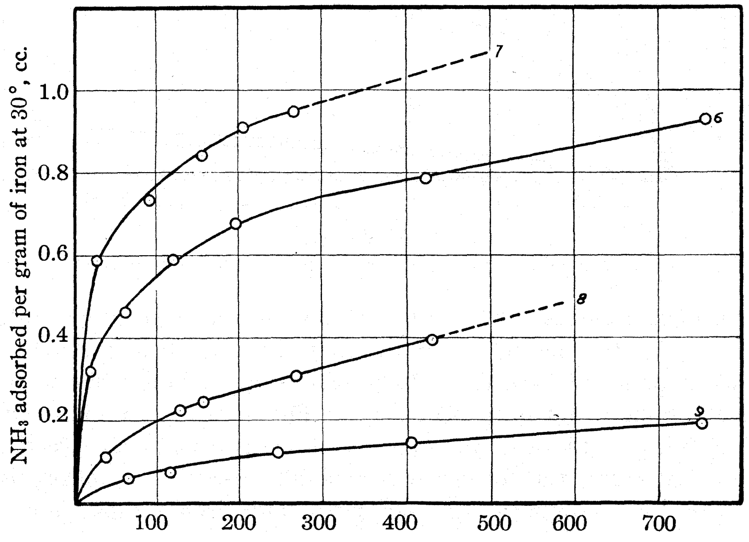

Fig. 2.—Adsorption of ammonia by pyrophoric iron.

It was previously[2] shown that samples of pyrophoric iron reduced from these oxides become non-pyrophoric when heated in nitrogen, hydrogen or helium at 600°. It was found that C became inactive the most rapidly, A next, B taking the longest time. On the basis of von Weimarn's precipitation rule, oxides C and A should have a greater degree of dispersion than oxide B. It was shown by Hofmann[3] that the extent of reduction of iron oxide depends among other factors upon the particle size of the oxide. From these considerations it seemed probable that the reason for the order of pyrophoric inactivation of the iron samples lay in the degree of incomplete reduction of the oxide, so that each particle or cluster contained a residual oxide core varying with the size of the original oxide particle. On this basis it seemed that pyrophoric iron B contained the largest oxide core while C contained the smallest. The definite order for adsorption of carbon dioxide and ammonia could thus be attributed to small amounts of oxide remaining as a core in the iron particles. Taylor and Burns[4] found that finely divided iron reduced from the calcined nitrate for twenty-six hours at 450° in hydrogen adsorbed only 0.25 cc. of carbon dioxide per cubic centimeter of iron. Nikitin[5] reports nearly 4 cc. of carbon dioxide adsorbed per gram of pyrophoric iron at 18° and 732 mm. Since the latter investigator prepared this iron by reducing ferrous carbonate in hydrogen at 515°, this high adsorption value may be attributed to residual oxide or carbon formed by the reaction of the carbon dioxide and iron. Pyrophoric iron produced from the carbonate, moreover, may contain more elementary spaces or fine capillaries[6] especially suitable for carbon dioxide adsorption.

Ammonia Synthesis

Since the iron prepared from oxide C was found to be very sensitive toward heating, becoming thereby non-pyrophoric very readily, and was also found to be inactive with' respect to adsorption, it was of especial interest to investigate the behavior of this particular iron in the synthesis of ammonia.

Materials

Gases.—Nitrogen and hydrogen were prepared by the thermal decomposition of ammonia by a method somewhat similar to that described by Larson, Newton and Hawkins,[7] the ammonia being passed over steel wool in a porcelain tube held at a red heat. The gases were purified by the method recommended by Larson and his co-workers.

Ferric Oxide B.—In addition to oxide B, previously described, "Oxide B-dialyzed" was prepared by precipitating oxide B, washing partially, dialyzing the precipitate in collodion bags for one week at 90–95° and finally drying.

Ferric Oxide C.—Together with the colloidal oxide C prepared by the method of Sorum[8] by hydrolyzing ferric nitrate and dialyzing the oxide so formed in collodion

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[3] Hofmann, *Z. angew. Chem.*, *38*, 715–721 (1925).

[4] Taylor and Burns, THIS JOURNAL, 43, **1276** (1921).

[5] Nikitin, *Z. anorg. allgem. Chem.*, 154, **130** (1926).

[6] Briggs, *Proc. Roy. Soc. London*, **100A, 88** (1921).

[7] Larson, Newton and Hawkins, *Chem. Met. Eng.*, *26*, **494–497** (1922).

[8] Sorum, THIS JOURNAL, 50, **1263** (1928).

bags, an oxide C was dialyzed in parchment bags. Oxide C *ex* $Fe(NO_3)_3$–$Al(NO_3)_3$ was also prepared by hydrolyzing 10 g. of ferric nitrate and 1 g, of aluminum nitrate in boiling water, dialyzing in collodion bags and treating subsequently like oxide C. The ignited oxide C *ex* $Fe(NO_3)_3$–$Al(NO_3)_3$ contained 95.4% of Fe_2O_3, the remainder being Al_2O_3. All oxides were ground to 5- to 12-mesh.

Method and Results.—The catalyst was prepared by reducing the desired iron oxide in the hydrogen–nitrogen mixture at 400–450° at one atmosphere pressure. The type of catalyst tube used was similar to that described by Almquist and Black.[9] All experiments were carried out at atmospheric pressure with 5000, 11,000 and 16,000 space velocities, 2 cc. of catalyst being used. The ammonia was absorbed in 0.1 N sulfuric acid and the excess acid titrated with 0.1 N sodium hydroxide, using methyl orange as an indicator.

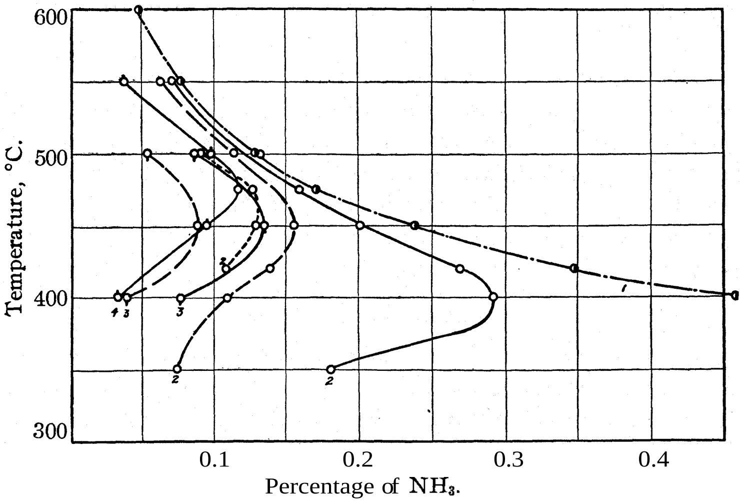

Fig. 3.—Curve **1**, equilibrium; **2**, oxide B; **3**, oxide B dialyzed; **4**, C *ex* $Fe(NO_3)_3 \cdot Al(NO_3)_3$: 5000 S. V.————, 11,000 S. V.— — —, 16,000 S. V.– – – – – –.

Oxide C was reduced at 400° for thirty-six hours and finally at 500°. This oxide proved to be absolutely worthless as a catalyst, no ammonia being formed. Upon examining the reduced oxide microscopically the granules of iron appeared not in the least porous but had a distinctly metallic luster, indistinguishable under a low power microscope from a piece of white cast iron. From the appearance of the iron, an extremely rapid recrystallization must have taken place; however, some poison from the collodion bags may have caused its inertness as a catalyst. To test the probability of poisoning, oxide B and oxide B-dialyzed were used as catalysts. The results obtained are presented in Fig. 3, showing that a cer-

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[9] Almquist and Black, This Journal, 48, **2814** (1926).

tain amount of inactivation was caused by dialysis since the curves for B-dialyzed lie a greater distance from the theoretical curve than those for catalyst B. With the view that collodion may have had a poisoning effect on iron C, oxide C was dialyzed in parchment bags. Here again no ammonia was produced, the iron after reduction having a decidedly metallic luster. If recrystallization forces caused the inertness of iron C, the incorporation of an oxide of the Al_2O_3 type in the catalyst should prevent such an occurrence. Wyckoff and Crittenden[10] have shown that such an oxide acts as a "guard," inhibiting sintering of the iron. Such a mixed oxide, C ex $Fe(NO_3)_3$–$Al(NO_3)_3$, was prepared and reduced in the same manner as oxide C. The mixture showed catalytic properties although it was not as active as iron B. The results are given in Table II and shown graphically in Fig. 3. After being in use for more than a day, the catalyst had a bulky black appearance in contrast to the metallic gray of iron C. The material was decidedly pyrophoric when thrown into the air. These experiments, together with the fact that pyrophoric iron C is easily caused to become non-pyrophoric upon heating, point to the fact that the sensitivity and ease of inactivation of iron C is due to extremely rapid recrystallization. The superior catalytic property of iron B could be attributed to the lower degree of dispersion of oxide B. Oxide B would be more difficultly reduced and the resulting iron particles no doubt would contain small oxide cores which tend to hinder coalescence of the iron in a manner similar to the action of aluminum oxide.

TABLE II

AMMONIA SYNTHESIS WITH PYROPHORIC IRON AS CATALYST

Ammonia Concentration—Per cent.

Temp., °C.	Oxide B, space velocity 5000	11,000	16,000	Oxide B-dial., space velocity 5000	11,000	C ex $Fe(NO_3)_3$–$Al(NO_3)_3$ space velocity 5000	Equilib.[11]
350	0.180	0.008	...	...	...	...	...
400	.290	.109	...	0.075	0.038	0.031	0.457
420	.269	.139	0.108	...	...	...	.347
450	.200	.155	.129	.133	.087	.091	.236
475	.159	.136	.126	...	...	.116	.170
500	.130	.112	.089	.088	.052	.098	.128
550	.070	.063	...	...	...	.037	.076

Summary

1. Adsorption of carbon dioxide by pyrophoric iron is no criterion for pyrophoric action, a sample of non-pyrophoric iron adsorbing more gas than a sample of pyrophoric iron.

2. Adsorption of carbon dioxide and ammonia by the samples of pyro-

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[10] Wyckoff and Crittenden, THIS JOURNAL, 47, 2866 (1925).

[11] Larson and Tour, *Ind. Eng. Chem.*, 26, 649 (1922).

phoric iron prepared seems to be dependent primarily upon the amount of residual oxide contained in the iron.

3. Iron prepared from colloidal iron oxide by Sorum's method was worthless as an ammonia catalyst. The incorporation of colloidal aluminum oxide in this colloidal iron oxide produced an active catalyst.

4. It appears as though inactivation of an iron catalyst through processes of recrystallization is hindered by an iron oxide core within the iron particles.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WASHINGTON]

THE EQUILIBRIUM OF THE REACTION BETWEEN NITROGEN AND CARBON DIOXIDE IN THE ELECTRIC ARC

BY H. V. TARTAR AND J. L. HOARD

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This study was undertaken as a natural consequence of former work performed in this Laboratory on the equilibrium of gaseous reactions in the electric arc.[1] The reaction between nitrogen and carbon dioxide seemed to offer a very interesting problem because of the appearance of *a* recent article[2] which indicated that a much higher concentration of nitric oxide could be obtained with a mixture of these gases than could be realized with a mixture of nitrogen and oxygen. The earlier work of Muthmann and Schaidhauf[3] seemed to indicate that this view is erroneous; for they obtained concentrations of nitric oxide from carbon dioxide and nitrogen mixtures which compare unfavorably with those obtainable from air. However, it seemed desirable to collect a more complete series of data in which conditions were varied and in which equilibrium was known to be realized.

Description of Apparatus.—The power supply available was 110-volt, SO-cycle alternating current. The high voltage necessary to maintain the arc was obtained by means of an oil-cooled, closed core transformer of 3.5 kilowatts capacity. Reactance coils in the primary circuit served to stabilize the arc and to give the desired value of secondary current. A milliammeter in the secondary circuit indicated the value of the current. The line voltage varied somewhat, but the current through the arc was substantially constant.

The arc furnace was that used by Colin and Tartar[4] in their study of the equilibrium of the reaction of nitrogen and oxygen in air and other mixtures, to form nitric oxide. It consisted of a 5-liter pyrex flask with platinum electrodes sealed into the neck of the flask. The electrodes were originally of the horn-gap type, and were about 0.8

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[1] (a) Tartar and Perkins, *J. Phys. Chem.*, **30**, 595–616 (1926); (b) Colin and Tartar, *ibid.*, 31, 1539–1558 (1927).

[2] Krase and Mackey, *ibid.*, **32**, 1488–1494 (1928).

[3] Muthmann and Schaidhauf, *Z. Electrochem.*, 17,497 (1911).

[4] Ref. 1b, see Fig. 2, p. 1544.

cm. apart, but at the temperature of the arc the platinum was gradually volatilized and fused down, so that only small hooks remained upon the ends. The neck of the flask was drawn out and sealed to a two-way stopcock, and another outlet was provided in the bottom of the flask. To each side of the two-way stopcock (a in Fig. **1)** was sealed a T-tube; one side of each T-tube was joined to a manometer and the other to a tube containing phosphorus pentoxide (b in Fig. 1). Nitrogen was admitted to the furnace through one of these drying tubes after having passed successively through alkaline pyrogallol, concentrated sulfuric acid and a tube containing heated metallic copper. This latter tube was closely packed with alternate layers of copper gauze, tightly wound into rolls, and of granulated copper. The copper was heated to a dull red during the passage of nitrogen; the oxide formed was periodically reduced with hydrogen.

The tube (e) was filled with carbon dioxide snow and by means of the by-pass (d-g) leading directly to a Cenco Hivac pump was subjected to direct evacuation until nearly one-half of it was gone. This served to purify the carbon dioxide by removal of the gaseous impurities. The purified gas was then admitted to the furnace after passing through the drying tube (b).

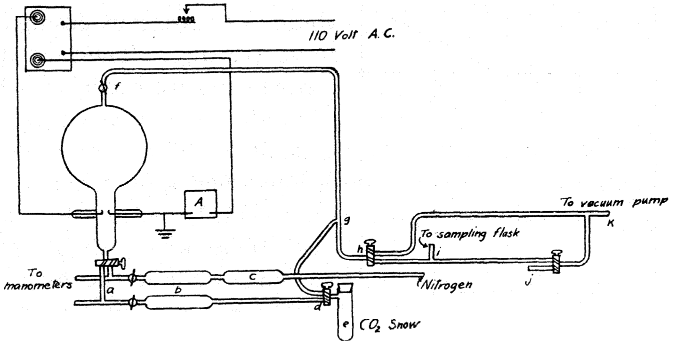

Fig. 1.

Between the points (h) and **(k)** (Fig. **1)** were two lines leading to the pump; one was used for evacuation; the other for sampling the reaction products. The sampling flask was connected in the line by means of a T (i in Fig. **1)** and was evacuated down to the limit of the pump when preparing for use. The sampling flask consisted of a 5-liter pyrex flask with a stopcock sealed into the bottom. An absorption train between (i) and (j) served to absorb residual gases after the sampling had been accomplished. Air was first admitted to oxidize the nitric oxide and the gases were then drawn through towers containing hydrogen peroxide and caustic soda solutions (in separate towers).

Method of Procedure

The furnace was evacuated by means of the direct line to the pump. It was then flushed out four times with the oxygen-free nitrogen and with the aid of the manometer in that line was filled to the desired pressure. Carbon dioxide snow was then introduced into the tube (e) and purified as described heretofore. The furnace was filled to the desired total pressure with carbon dioxide. The arc was started and allowed to run for at least three hours, although tests indicated that equilibrium essentially was attained in a somewhat shorter period. At the end of this time a sample of the reaction gases was drawn for analysis. The sampling flask was evacuated and the gases were allowed to distribute themselves through the system, When constant pressure and temperature had been attained, the flask was withdrawn, sodium hydroxide solution was drawn into it (since it was still under reduced pressure) and air was admitted to oxidize the nitric oxide. The flask was allowed to stand with occasional vigorous shaking until the nitrous gases were completely absorbed. The solution was then washed into a 500-cc. Kjeldahl flask and the nitrogen compounds reduced with Devarda's alloy to ammonia, which finally was distilled into standard sulfuric acid. In order to avoid carrying over alkali spray during the distillation, an apparatus was used which was quite similar to that of Mitscherlich.[5] This method was found to be quite reliable. All results were calculated as percentage of nitric oxide by volume of the actual amount of gas present in the furnace.

Discussion

The equation for the reaction of nitrogen and carbon dioxide to form nitric oxide may be written

$$N_2 + 2CO_2 = 2NO + 2CO$$

Thus a two-to-one mixture of carbon dioxide to nitrogen should, theoretically, give the best yield of nitric oxide. Also, it is apparent that three volumes of reacting gases give four volumes of reaction products at constant pressure. The fact that these experiments were performed at substantially constant volume made it difficult to obtain exactly similar conditions when approaching the equilibrium from both sides for, in the one case, there was a slight increase in pressure, while in the other there was a slight decrease. Furthermore, when equilibrium was attained, starting with a nitrogen–carbon dioxide mixture, there was undoubtedly some excess of oxygen and of carbon monoxide present, resulting, of course. from the decomposition of some carbon dioxide not taking part in the reaction with nitrogen; this amount was not precisely known. However, starting with 5% of nitric oxide and 5% of carbon monoxide, with 60% of carbon dioxide and 30% of nitrogen, it was possible to arrive at an equilibrium mixture differing by but 0.1–0.2% from that reached when starting with the theoretical mixture of carbon dioxide and nitrogen. Carbon monoxide was generated by dropping formic acid into concentrated sulfuric acid; nitric oxide by dropping dilute nitric acid through copper gauze so as to keep the nitrate solution formed out of contact with the metal.

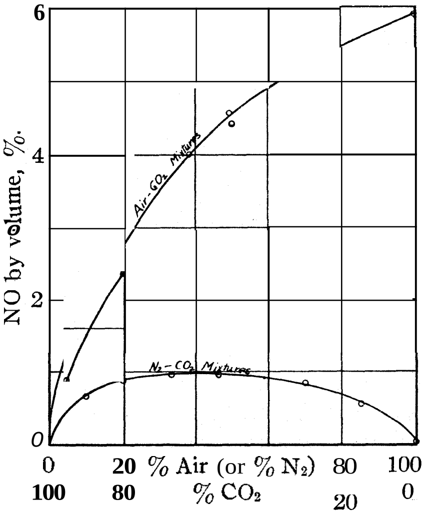

Fig. 2.

A series of runs was made with a current of 65–67 milliamperes and at 760 mm. pressure, in which mixtures of air and carbon dioxide ranging

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[5] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 1922.

from 100% of the former to 95% of the latter were used. The results are reported in Table I and are shown graphically in Fig. 2. These data indicate that carbon dioxide acts largely as a diluent under these circumstances, for the concentrations of nitric oxide obtained range from 1.3% in a mixture containing 95% of carbon dioxide, to 5.9% for pure air. This view is substantiated for the most part by the results obtained from nitrogen–carbon dioxide mixtures under similar conditions of current and pressure. The data are given in Table II and are plotted in Fig. 2. Here a maximum of about 1% of nitric oxide was obtained, or only one-sixth the concentration resulting from air alone. In all runs but those having

TABLE I

NITRIC OXIDE FROM AIR AND CARBON DIOXIDE MIXTURES

Run	Pressure, mm.	Current, m. a.	Air, %	Carbon dioxide, %	Nitric oxide, %
N-3	760	67	100.0	0.0	5.92
N-4	760	66.5	80.0	20.0	5.46
N-9	760	67	50.6	49.4	4.43
N-2	760	66.5	50.0	50.0	4.57
N-8	760	65	39.1	60.9	4.02
N-1	760	66	20.0	80.0	2.76
N-7	760	66	5.0	95.0	1.30

TABLE II

NITRIC OXIDE FROM NITROGEN AND CARBON DIOXIDE MIXTURES

Run	Pressure, mm.	Current, m. a.	Nitrogen, %	Carbon dioxide, %	Nitric oxide, %
J-1	760	67	100.0	0.0	0.028
J-6	760	66	100.0	0.0	.014
J-8	760	66	85.0	15.0	.55
J-2	760	67	70.0	30.0	.85
J-4	760	66	46.2	53.8	.95
J-3	760	66.5	33.3	66.7	1.00
J-7	760	66	33.3	66.7	0.94
J-5	760	66	20.0	80.0	.88
J-9	760	65	10.0	90.0	.66
L-4	500	66	85.0	15.0	.83
L-6	500	66	70.0	30.0	.945
L-3	500	67	64.4	35.6	.845
L-2	500	66.5	50.0	50.0	1.03
L-1	500	67	33.3	66.7	0.99
L-5	500	66	14.6	85.4	.83
K-4	300	67	85.0	15.0	.41
K-3	301	67	64.4	35.6	.78
K-2	300	66	50.0	50.0	.93
K-1	301	67	32.2	67.8	.89
K-5	300	68	15.0	85.0	.79
M-3	150	66	65.0	35.0	.99
M-2	150	67	47.3	53.7	1.03
M-1	150	67	33.3	66.7	0.91
M-4	150	66	33.3	66.7	1.13

the highest percentages of nitrogen, the presence of the brown color of nitrogen dioxide demonstrated that some carbon dioxide had been decomposed beyond that required by the foregoing equation. Thus there is also the equilibrium between carbon dioxide and its dissociation products to be considered.

TABLE III

NITRIC OXIDE FROM NITROGEN AND CARBON DIOXIDE MIXTURES

Run	Pressore, mm.	Current, m. a.	Nitrogen, %	Carbon dioxide, %	Nitric oxide, %
0-4	760	97	85.0	15.0	0 82
0-3	760	97	70.0	30.0	0.98
0-2	760	98	50.0	50.0	1.16
0-1	760	99	33.3	66.7	1.23
0-8	760	97	30.0	70.0	1.38
0-5	760	97	20.0	80.0	1.36
0-6	760	98	20.0	80.0	1.33
0-7	760	97	10.0	90.0	1.15

Since Colin and Tartar[1b] had shown that high concentrations of nitric oxide could be attained at reduced pressures from air and other nitrogen–oxygen mixtures, it was decided to try a similar proceeding with nitrogen and carbon dioxide. Series of runs were made, therefore, at 500, 300 and 150 mm. pressure. The results are given in Table II and the first two are compared graphically with the atmospheric runs made with the same current in Fig. 3. The values determined at 150 mm. are altogether too uncertain to more than indicate the order under those conditions. The effect of pressure upon the equilibrium between nitrogen and carbon dioxide seems to be rather slight; in fact, there is scarcely more than 0.1% variation, and this almost comes within the limits of experimental error. As a matter of fact, the two values obtained at 500 mm. pressure with original concentrations of nitrogen of 70 and 85% are, perhaps, a little high for the reason given in the next paragraph. Pressures above atmospheric were not tried, but it seems improbable that the reaction would be much favored, if at all, by such a procedure.

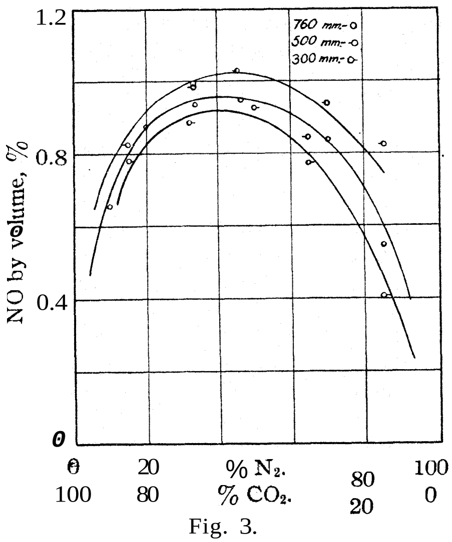

Fig. 3.

Finally, a series of runs was made at atmospheric pressure with a somewhat larger current. Unfortunately this increased current (about 98–100 milliamperes, or approximately a 50% increase) proved to be more than the electrodes could conveniently handle, and the "horn-gap" was completely fused down into stubs. This, of course, had the effect of increasing the current density for the same current. Therefore, this last series is not quite so consistent as those made with the lower current. (The two values made at 500 mm. and 65 milliamperes referred to above as being somewhat high were made after this change in the electrodes.) It was found, however (Table 111), that 50% increase in current caused 30–40% increase in the concentration of nitric oxide.

The natural inference from the foregoing results is that not nearly as high a concentration of nitric oxide can be produced by the high tension electric arc from carbon dioxide and nitrogen as can be produced from air or other nitrogen-oxygen mixtures. Krase and Mackey[3] have recently published some thermodynamic calculations which seem to indicate that the very opposite is true, *e.* g., that four times as high a concentration of nitric oxide could be produced from carbon dioxide and nitrogen mixtures at 3500°, as would be obtained from air. They gave (at 3500°) 5.52% nitric oxide for air, and the present work shows 5.9%, corresponding to some unknown temperature; but where their calculations for nitrogen–carbon dioxide mixtures indicate 23.75% (at 3500°) and 10.88 (at 3000°), the present work shows not more than 1.4%. Now the matter is somewhat complicated by two factors: first, the temperature of the arc (or of the region at the edge just outside the arc where a thermal equilibrium is attained),[6] and, second, the rapidity with which the equilibrium is "frozen." The work of Colin and Tartar[1b] showed that such an equilibrium is "frozen" with almost incredible rapidity. It appears, therefore, that if an equilibrium be attained at some high temperature, say 3000°, it should be little changed during cooling. With this fact established, only the question of the temperature to which the equilibrium corresponds remains to be considered.

In the case of air, it is seen from a comparison with the data of Nernst, Finckh and Jellinek[7] for a purely thermal equilibrium that the concentration of nitric oxide here obtained must correspond to a very high temperature. At 2675° they found 2.23% of nitric oxide (although it appears from the more recent data of Briner, Boner and Rothen[8] that this value may be somewhat low). As a matter of fact, Nernst, Finckh and Jellinek, by extrapolation from their experimental data, estimate that the temperature corresponding to a thermal equilibrium concentration of 6% nitric oxide

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[6] Daniels, Keene and Manning, Trans. Am. Electrochem. *Soc.*, 44,247 (1923).

[7] Nernst, Finckh and Jellinek, Z. *anorg. Chem.*, 45, 116–126 (1905); 49, 213–229 (1906).

[8] Briner, Boner and Rothen, J. *chim. phys.*, 23, 788 (1926).

is approximately 3500 Å.; and about 6% was obtained in the present work. It seems justifiable, furthermore, to assume that the equilibrium with carbon dioxide–nitrogen mixtures corresponds to a temperature comparable with that in the case of air, particularly in the cases where the current was increased by 50% over that used for air. Moreover, Colin and Tartar[1b] found, in the case of air, that the highest concentrations of nitric oxide were obtained at relatively low values of current, that is, 40 milliamperes or less, so it is improbable that the yield of nitric oxide from nitrogen–carbon dioxide mixtures could be improved by indefinitely increasing the current. The conclusion is, therefore, that only small concentrations of nitric oxide, as compared with air, may be produced from nitrogen–carbon dioxide mixtures in the high tension arc.

The validity of the calculations of Krase and Mackey[2] appears to be in question. One objection to their procedure is the empirical equations used for expressing heat capacity as a function of the temperature. The equations for the heat capacities of nitrogen, oxygen, nitirc oxide, carbon monoxide and carbon dioxide apparently were taken from Lewis and Randall[9] who had formulated them upon the basis of data collected from various sources.[10] These equations, admittedly of a grossly empirical character, and based upon a minimum of reliable experimental data, have been used in the calculations of Krase and Mackey over a temperature range which amounts to an extrapolation of 1000–1500". This is, no doubt, an unjustifiable procedure; for it is the opinion of Partington and Shilling,[11] who have recently collected data on the heat capacity of gases, that practically no reliable information exists for the region above 2000°. They state: "It will be seen, too, that the tables do not extend above 2000". This is admittedly a drawback, but reliable tables cannot be constructed for the region where practically no accurate data exist. For approximate estimations in the region 2000–3000°C., several indications may be given, but that is all. For example, the molecular heats of the so-called permanent gases probably reach a maximum value, and continue for some considerable temperature range at that value. . . . It must be emphasized, however, that the final equations given for these tables apply only over the temperature range stated. Extrapolation will not give accurate results. . . ."

Summary

1. Only small concentrations of nitric acid were produced from nitrogen–carbon dioxide mixtures in the electric arc.

2. With a current of 65 milliamperes only one-sixth (1%) the concentra-

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

[10] Lewis and Randall, THIS JOURNAL, 34, 1128 (1912).

[11] Partington and Shilling, "The Specific Heats of Gases," Ernest Benn, Ltd., London, 1924.

tion of nitric oxide was produced from nitrogen and carbon dioxide as was produced from air.

3. The effect of reduced pressure upon the equilibrium obtained was very slight.

4. The results obtained show that the concentration of nitric oxide produced from carbon dioxide–nitrogen mixtures was increased by 30–40% when the current was increased by **50%.**

5. The results obtained show that the reaction between nitrogen and carbon dioxide holds little promise as a means of fixing nitrogen by the arc process.

SEATTLE, WASHINGTON

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

THE ORIGIN OF PROTOACTINIUM

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The major part of this investigation grew out of work started several years ago to separate protoactinium from America's most important uranium ore, carnotite. As expected, after much preliminary work, the presence of protoactinium was established. From the standpoint of radioactivity, it is generally considered as being the parent of actinium and hence takes its place at the head of the actinium series. The fact has long been established that the radioactive elements allow themselves to be arranged in three great divisions, the uranium, the thorium and the actinium series. The exact relation of the actinium series to the uranium and thorium series of radioactive elements is as yet not definitely known. This investigation was undertaken with the hope of throwing some light on this very important relationship.

The uranium disintegration series, as it is now generally represented, shows the actinium series as springing from uranium II, by the way of uranium Y, although it is generally indicated that this is uncertain.[1] According to this scheme, the actinium series is formed in a dual a-ray change from uranium II, the remainder of the uranium II atoms forming the ionium–radium series. At present the most widely accepted percentages for the numbers of uranium atoms forming the ionium–radium and actinium series are ninety-seven and three per cent., respectively. Obviously, if a definite percentage of the uranium atoms disintegrates to form the actinium series, the ratio between this series, or any member of it, to uranium, should be a constant in uranium bearing minerals, just as the radium–uranium ratio is constant.

[1] Meyer and Schweidler, "Radioaktivitat," **1927,** p. **347;** also Kohlrausch, "Radioaktivitat," **1928,** p. 8.

If, on the other hand, protoactinium exists in a series independent of uranium, the protoactinium–uranium ratio should show some variation in different minerals used as sources of protoactinium. While it is true that the proportion of the isotopes of stable elements, such as chlorine, is relatively constant in nature, it does not follow that constancy of proportion holds for radioactive isotopes, since their disintegration constants are generally quite different.

Boltwood[2] showed that the actinium content of minerals is roughly proportional to their uranium content. Fussler[3] measured the same relation for three different samples of carnotite and obtained values that are in the ratio 1.261 : 1.644 : 1.00. Meyer and Hess[4] made similar determinations on different uranium minerals and came to the conclusion that the actinium–uranium ratio is constant. Others[5] have made similar determinations on the uranium Y–uranium and the actinium series–uranium relations and report values ranging all the way from two to five per cent. When the results of all these investigations concerning this ratio are compared, the degree of variation is so marked that we cannot, even today, say with certainty that the ratio between the actinium series, or any member of it, and uranium, is constant.

The results of this investigation indicate that the protoactinium–uranium ratio is far from constant, and consequently strengthens the view advocated in recent years by several investigators that the actinium series is not a direct offspring of the uranium series. This conclusion is based upon the quantitative determination of the protoactinium–uranium ratio of different uranium minerals from widely separated localities. A rich carnotite from Colorado, two pitchblendes from Bohemia, a soddite from the Belgian Congo, and a thorianite from Ceylon, were analyzed for their protoactinium and uranium contents.

Preliminary Work.——First a method had to be developed for the quantitative separation and recovery of tantalum from carnotite, since tantalum is the nearest homolog of protoactinium and must be added to protect the minute quantities of protoactinium to be extracted. After obtaining confidence in the technique involved, an extensive amount of work still remained to be done on simplifying and standardizing a method, applicable not only to carnotite but, with little modification, to other uranium minerals as well.

In attacking a problem of this sort one naturally begins with methods which earlier investigators have followed in extracting protoactinium from uranium minerals. Hahn and Meitner[6] in their extended study of proto-

[2] Boltwood, *Am. J. Sci.,* [4] 25, 269–298 (1908).

[3] Fussler, Phys. *Rev.* [2] 9, 142–147 (1917).

[4] Meyer and Hess, *Sitzb. Wien. Akad.,* 128, 2a, 909–924 (1919).

[5] Kohlrausch, "Radioaktivitat," 1928, p. 757.

[6] Hahn and Meitner, Ber., 52, 1812–1828 (1919).

actinium, confined themselves to pitchblende as a source of the element. They used three different methods of extraction: (1) decomposition of the ore with sodium bisulfate, which leaves the protoactinium in the insoluble residue; (2) treatment with fifty per cent. hydrofluoric acid plus sulfuric acid, which puts the protoactinium into solution; and (3) the nitric acid treatment, which leaves most of the protoactinium in the insoluble residue.

For the preliminary work of separating protoactinium from carnotite the bisulfate method of Hahn and Meitncr seemed best adapted because, in their hands, better results were more readily obtained by it than with the other two methods.

The bisulfate method is, briefly, as follows: A few milligrams of tantalic oxide is added to the sample of mineral and the whole thoroughly fused with sodium bisulfate. The fused mass is then thoroughly lixiviated with boiling water, to which sulfur dioxide is added to aid in the quantitative precipitation of the tantalum. Upon filtering, radium, radio-lead, tantalum, protoactinium and small quantities of radium E, polonium, ionium and uranium X remain in the residue and uranium, ionium plus uranium X, actinium, radium E and polonium in the filtrate. The residue is now ignited in a porcelain crucible and then transferred to a platinum dish. Hydrofluoric acid, a few drops of sulfuric acid and a few drops of thorium nitrate solution are now added and the solution warmed on a water-bath. The tantalum and protoactinium are brought into solution in from one to two hours. Filtering through a paraffined funnel leaves radium, radio-lead, and traces of ionium plus uranium X in the residue, and tantalum, protoactinium and traces of radium E and polonium in the filtrate. The filtrate is now brought to the fuming point of the sulfuric acid and the residue treated with aqua regia to remove the last traces of radioactive impurities. The insoluble material left after the aqua regia treatment consists of the oxides of tantalum and protoactinium.

Hahn and Meitner refer to the fact that they had great difficulty in removing the tantalum from the platinum dish after bringing the solution to the fuming point of sulfuric acid, just before the aqua regia treatment. They solved the problem by adding a small quantity of an iron salt to the solution just before bringing it to the fuming point. This put the residue in a form less difficult to remove from the dish. The writer found that the tantalum, in the absence of an iron salt, is not only difficult to remove, but tends to form a glaze, especially around the side of the dish, which because of its transparency makes most of the residue invisible; but if water is added at this point and the surface of the dish carefully rubbed with a horn spatula, the glaze of tantalum comes off and forms a white suspension of tantalic acid. With a little patience all of the tantalum may be removed from the dish without the addition of an iron salt. In some cases as high as ninety-five per cent. of the tantalum was recovered from the pitchblende samples in this way.

Carnotite.—Carnotite is a potassium urano vanadate and even high grade material is very rich in silica. Consequently it was found very difficult to apply this method satisfactorily, for when the bisulfate fusion is made, the tantalum remains with the silica in the insoluble residue. After sufficient hydrofluoric acid had been added to remove all of the silica and put the tantalum in solution, nothing like quantitative returns could be made on the tantalum, because a considerable quantity of the tantalum is volatilized in the hydrofluoric acid treatment.[7] It was found in later experiments with other minerals, where much less silica was involved and hence much less hydrofluoric acid used, that the recovery on tantalum increased. However, the tantalum recovered from the carnotite by this method showed an increase in activity characteristic of protoactinium.

In the earlier experiments the recovered tantalum was badly contaminated with radium, which persisted very strongly. The barium in the carnotite remained in the insoluble residue, and a relatively large amount of it would be carried through with the hydrofluoric acid, since barium fluoride is far more soluble than barium sulfate.

Tantalum can be freed from radium by a procedure based on two findings: one is that freshly precipitated tantalic acid is very soluble in very dilute hydrofluoric acid, and the other is that tantalum is readily precipitated, even from solutions of hydrofluoric acid, by means of ammonium hydroxide.[8] The writer found that quantitative recoveries could be made in this way, especially in the presence of the small amount of hydrofluoric acid used in these separations. The mineral sample, to which the tantalic oxide had been added, was fused as before, boiled in a large excess of water and the solution filtered through a paraffined funnel. A beaker containing ammonium hydroxide was placed under it and some very dilute hydrofluoric acid poured through the precipitate. The tantalum, some silica and perhaps a little barium fluoride were carried through into the ammonium hydroxide. The tantalum immediately precipitated, and if much silica is present, it is precipitated at this point. Under any condition, much of the silica is carried into the filtrate, and the amount of hydrofluoric acid necessary to remove it will cause the yield of tantalum to be low. The operation of dissolving the tantalic acid from the residue on the filter paper with dilute hydrofluoric acid and precipitating it with ammonium hydroxide must, therefore, be repeated several times. This procedure has the advantage of not precipitating any of the barium and

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[7] Travers, *Compt. rend.*, 166, 494 (1918).

[8] Hopkins, "Chemistry of the Rarer Elements," D. C. Heath and Co., 1923, p. 235.

radium along with the tantalum, because ammonium hydroxide will not precipitate barium from dilute solutions of barium salts.

By several repetitions of the above operation, the tantalum precipitate is completely freed from traces of barium and radium salts. The tantalum precipitate is finally filtered, washed and ignited. Traces of silica are removed with hydrofluoric acid. For final purification, and to give the precipitate a good texture, it is fused with potassium bisulfate and the melt dissolved in boiling water. After filtering, washing and igniting, the tantalic oxide comes out as a fine, white powder which is easily brushed from the crucible.

With these modifications, the recoveries from carnotite were much better than those obtained by the Hahn and Meitner method, and the separations, in the main, less difficult to carry out. Even with all of the above precautions, it is difficult to remove the last traces of radium. This was verified time and time again during the course of this investigation. Since the amount of protoactinium is determined by the activities of these tantalum preparations, it is very important to rid them entirely of other active material. Because of the generally low recoveries made on the tantalum by fusion with bisulfate, it was reluctantly abandoned.

The procedure finally employed for the extraction of protoactinium from carnotite was developed from a method used by Russell and Widdowson[9] for the extraction of protoactinium from pitchblende. By introducing some modifications, the Russell and Widdowson method can be applied not only to carnotite, but to other uranium minerals as well. Their method is, briefly, as follows. The mineral sample is boiled vigorously for an hour in dilute nitric acid and then filtered. The residue is active. A few milligrams of tantalic oxide is added to this residue and the whole mass fused with potassium hydroxide in a nickel crucible. The melt is dissolved in cold water and the residue, which is inactive, is filtered out. The alkaline solution is now added to the nitric acid solution, then a few cubic centimeters of dilute sulfuric acid and the solution is neutralized with ammonium hydroxide. Upon boiling, the tantalum separates out as a flaky precipitate. The precipitate is filtered out, washed, and then fused with potassium bisulfate to remove elements other than those of atomic number ninety-one. Naturally, some modification must be made here for minerals such as carnotite, which contains considerable barium, and at the same time have a high silica content.

In this procedure the silica is all changed to the soluble silicate in the potassium hydroxide fusion and then when the alkaline solution is added to the nitric acid solution, great quantities of silicic acid are precipitated, from which it is very difficult to separate the small amount of tantalum. In fact, it is almost impossible to separate quantitatively the small amounts of tantalum, if there is much silica present.

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[9] Russell and Widdowson, *Phil. Mag.*, 46, **925 (1923).**

It was found in the course of this work, that in order to get quantitative returns on the tantalum, it was necessary to add ammonium hydroxide until a small amount of the uranium, and perhaps a little vanadium, were precipitated along with the tantalum. The uranium and vanadium were removed later. As to final fusion with bisulfate, carnotite presents a problem because of the presence of barium. It is obvious that barium cannot be removed by fusion with bisulfate.

In order to utilize the fusion with potassium hydroxide for the extraction of tantalum from carnotite, it is evident from all the preceding work that most of the silica must be first removed from the mineral sample. To this end, the radioactive constituents of the mineral were concentrated, before adding the tantalum to protect the protoactinium in carnotite, by sliming with dilute nitric or sulfuric acid, which leaves the bulk of the sand in an inactive residue. It was found that the sand was inactive only after sliming off about six times and only the coarsest sand remained. Small quantities of silica carried over in this operation gave no particular trouble in the precipitation of the tantalum and they were finally removed with hydrofluoric acid. In fairness to the bisulfate method of Hahn and Meitner, it may be said that great quantities of silica in all methods investigated gave serious trouble.

The best results were obtained when carnotite was dissolved in about twenty per cent. sulfuric acid instead of dilute nitric acid, using about ten cubic centimeters of the acid per gram of sample and sliming off as indicated above. The main advantage of using sulfuric instead of nitric acid lies in the fact that sulfur dioxide reduces vanadic salts very readily in the presence of sulfuric acid, but not in the presence of nitric acid. It was found that tantalum precipitates much more readily and in better form in the presence of the reduced vanadium salts. The solution was filtered and the tantalic oxide added to the dried residue and fused with potassium hydroxide in a nickel crucible. After the fusion was dissolved in cold water, there was practically no evidence of a precipitate and it was not filtered. The alkaline solution was then added to the acid solution and sulfur dioxide passed in until the vanadium was reduced to a lower state of valence, as indicated by the change in color. Ammonium hydroxide was added to incipient precipitation of uranium and perhaps some vanadium, and the solution boiled to precipitate the tantalum. Traces of barium sulfate and other insoluble sulfates appear immediately and later on the tantalum precipitates in a form which settles readily.

A difficulty here is apparent, that is, the barium–radium sulfates are brought down with the tantalum. Any number of bisulfate fusions would not remove the barium, The problem of separating the radium from the tantalum here offered one of the greatest difficulties of all in the work on carnotite. At first an attempt was made to remove most of the barium sulfate by letting it settle out before boiling the solution to precipitate the tantalum. After the solution had stood for forty-eight hours, it was decanted and filtered from the insoluble sulfates and the tantalum precipitated in the filtrate. This, on six different samples, showed that even in the cold about four-fifths of the tantalum was carried down with the barium sulfate.

Since the barium sulfate carries down most of the tantalum, even in the cold, there is no gain in trying to remove most of it by letting it settle out prior to boiling to precipitate the tantalum. On the contrary, it is best to boil the solution and precipitate the tantalum immediately after adding the ammonium hydroxide. The precipitate, consisting of tantalic acid, barium sulfate, some silica and so forth, may be allowed to settle and most of the supernatant liquor decanted before filtering, or it may be filtered through paraffined funnels as soon as it is cool, and treated with dilute hydrofluoric acid and ammonium hydroxide, as described under the bisulfate method.

In order to determine how many precipitations by the ammonium hydroxide would be necessary to remove the radium, the following experiment was carried out. Three ten-gram samples of carnotite were carried through the above procedures and filtered into paper cartons lined with paraffin. These filtrates were each diluted to about one hundred cubic centimeters and a little barium chloride solution was added to each. Since the sulfate is much more insoluble than the fluoride, a few drops of dilute sulfuric acid was added to each of them, and then each solution stirred with a platinum wire. The precipitate of barium sulfate and barium fluoride was allowed to settle for at least forty-eight hours, and then the solution was filtered through a good quality of filter paper and thoroughly washed. These papers were flattened out, dried and then placed in the chamber of an α-ray electroscope. In this particular instrument they had an average activity of 169.5 divisions per minute, and all ran very closely the same. The solutions were again treated with barium chloride and sulfuric acid, as before, and again allowed to stand for forty-eight hours. After filtering, washing and drying, the residues had the following activities in divisions per minute: No. 1, 0.13; No. 2, 3.35 and No. 3, 8.66. These divergencies are to be expected since no special care was used in the preparation of the films. They would normally, under the conditions, vary in concentration, area and thickness. After a third treatment, as outlined above, except that this time they were filtered through two thicknesses of filter paper, they had the following activities, in divisions per minute: No. 3, practically no activity on either filter paper; No. 2, 0.75 on the upper paper and 0.087 on the lower paper and No. 3, practically no activity on either filter paper. After a fourth treatment there was negligible activity in all three samples. The solutions were now made ammoniacal and the tantalum precipitated. This clearly indicates that if the tantalum is precipitated in the presence of the barium and radium carried through by the hydrofluoric acid treatment of the original residues, it is contaminated, and would certainly give untrustworthy results. In all of the experiments the results of which are recorded in this paper, the above operation was carried out from four to five times, depending on the mineral. By careful work, it is easy to recover upwards of ninety per cent. of the tantalum.

Thorianite.—The method of Russell and Widdowson, modified as indicated above, readily lends itself to thorianite. After grinding the mineral, it is treated with about forty per cent. nitric acid, using fifteen cubic centimeters of the acid per gram of sample. By gentle heating it is easily put into solution in less than a half hour. The solution is diluted, filtered and the residue dried and fused with potassium hydroxide in a nickel crucible. The tantalic oxide is added to the potassium hydroxide fusion. When quantitative results are desired, it is best to fuse the potassium hydroxide until vigorous action ceases and then drop the tantalic oxide into the crucible. It may be carefully brushed in, or put into a small piece of paper and dropped in. This procedure lessens the danger of losing any of the tantalum during the vigorous part of the reaction. The heating is continued until there is complete fusion, and since this tantalum is to bring out all of the protoactinium, it is best to keep it in a state of fusion at least fifteen minutes. The melt, after it has cooled, is dissolved in cold water. In the case of thorianite, the precipitate formed when the potassium hydroxide fusion was dissolved in water was very small, and since it was found to be very soluble in nitric acid, it was not removed. The potassium hydroxide solution is now added to the original nitric acid solution, then a few cubic centimeters of dilute sulfuric acid, and ammonium hydroxide to incipient precipitation of the uranium and thorium. The tantalum readily precipitates after boiling the solution for a few minutes. Since this particular mineral was relatively rich in radium, the tantalum precipitate was dissolved in hydrofluoric acid and precipitated with ammonium hydroxide, and this operation repeated four times in order to remove the last traces of radium. The final precipitate of tantalum was dried and fused with potassium bisulfate and the silica removed with hydrofluoric acid. The residue was finally weighed as tantalic oxide.

Soddite.—Soddite is a combination of uranic oxide, silica and water of hydration. It was treated in precisely the same way as thorianite. It required about three quarters of an hour to bring it into solution. In order to get the tantalum to precipitate, ammonium hydroxide must be added until considerable uranium is brought down and the precipitate is quite bulky. This precipitate is filtered out, ignited and then treated with nitric acid. The reason for igniting it is to change the tantalic acid to tantalic oxide, as freshly precipitated tantalic acid is quite soluble in mineral acids. The greater part of this ignited precipitate went into solution in the nitric acid. The residue remaining from the nitric acid treatment was filtered, washed and fused with potassium bisulfate, mainly to bring the tantalum into **a** condition in which it is readily soluble in dilute hydrofluoric acid. Upon boiling the bisulfate fusion in water, the tantalum readily separates out. This solution was filtered through a paraffined funnel, the precipitate washed and repeatedly treated with hydrofluoric acid and ammonium hydroxide as in the case of other minerals. The precipitate was finally thoroughly washed, dried and the silica removed in the regular way. To obtain a better texture, it was fused with potassium bisulfate, leached out and finally ignited to tantalic oxide.

Pitchblende.—The pitchblendes were treated in precisely the same way as the thorianite. The lead sulfate was more marked in the pitchblende than in the other minerals, because of their much higher uranium content. In all cases, the repeated treatment of the precipitates with dilute hydrofluoric acid and ammonium hydroxide removes the lead. This treatment also puts the tantalum through the same chemical processes as were followed with the other minerals. As with the other minerals, the tantalum precipitate was finally fused with potassium bisulfate, not only to purify it, but to put it into better form. In all this work samples ranging from three grams, in the case of pitchblendes, to ten grams in the case of carnotite, were used.

With all the minerals studied, the method outlined above gave excellent quantitative results when one considers the great number of chemical manipulations involved and the recovery of the twenty milligrams of tantalic oxide which was added in each case. In most cases upwards of ninety per cent. of the tantalum was recovered, and in many cases the recoveries were considerably higher than this. While it is important to obtain good quantitative results, it is more important to see to it that the samples have been fused long enough to bring the tantalum in contact with all of the protoactinium. Fundamentally, a quantitative return on the tantalic oxide added to the sample is unnecessary, if the recovered oxide is pure. The activities of the films made from the tantalic oxide recovered depends on the amount of protoactinium present in the sample, hence the activity due to all of the protoactinium in the sample of mineral can be computed from films of known weight, provided the weight of the tantalum added to the original sample is known. The total activity, divided by the weight of the sample in grams, gives the activity due to the protoactinium in one gram of the mineral.

To prove that the activities of the protoactinium films furnish a true measure of the quantity of the protoactinium in minerals, the following sets of separations were carried out. The protoactinium was separated from three different minerals, using samples of different weight, but adding the same weight of tantalic oxide to each sample. Uraninite, thorianite and carnotite were used in these tests. For uraninite and thorianite, three three-gram and three six-gram samples were used. For carnotite, three five- and three ten-gram samples were taken. Twenty milligrams of tantalic oxide was added to each of the eighteen samples and then the samples were processed as described.

Films of the tantalic oxide recovered from each sample were made, weighed and their activities measured. From the weight of the film and its activity, the activity of twenty milligrams of film was computed. This value represents the a-ray activity of all the protoactinium in the sample of mineral taken.

Normally the tantalic oxide recovered from the larger samples should be twice that from the smaller samples and the activity per gram of mineral should be constant for each mineral, but different for the different minerals.

The averages of the total activities, in divisions per minute, and the ratio of the two activities, are given in the following tabulation.

Mineral	Av. small samples	Av. large samples	Ratio
Uraninite	7.46	15.32	2.05
Thorianite	4.31	9.40	2.18
Carnotite	8.73	17.66	2.02

The individual readings vary from 3.6 to 12.9% from the average readings given above. The eighteen samples were put through the same chemical processes as nearly as possible. Except in the case of the inactive sand from carnotite, the tantalum was precipitated in the presence of the whole sample in solution, that is, there was no chance for the division of the protoactinium between residue and solution in any stage of the analysis. The double quantity of protoactinium extracted when the mineral samples were doubled clearly established the reliability of the method followed for the quantitative separation of protoactinium from different types of uranium minerals.

The activities of the numerous protoactinium preparations obtained in this investigation were measured in an a-electroscope. The general idea for the use of the films was taken from Boltwood.[10] The material to be measured was painted on thin aluminum disks eight centimeters in diameter. These disks were turned in such a way as to have a rim about one millimeter high. The rim not only protects the film to some extent, but it keeps the very thin disk perfectly flat. The rims were so low that no correction was made for a-particles that may have encountered them. Before shaping the disks, one surface of the thin sheet aluminum was thoroughly rubbed with steel wool. This surface was then rubbed with

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[10] Boltwood, Am. J. *Sci.,* [4] **25,** 176 (1908).

clean cotton until all free particles of aluminum were removed. This treatment produced a very slightly roughened surface upon which films can be painted more uniformly than on smooth aluminum. Material to be painted on these disks was ground very fine in an agate mortar and a suspension formed by adding a few drops of acetone. After trying different methods for painting films on these disks, it was found that small tufts of cotton, tightly rolled and held with small tweezers, were as good as anything tried. A small camel's hair brush works fairly well, except that in using the very small amount of material necessary in this work, practically all of it would be drawn up into the brush. Then too, a new brush would be required for each new preparation because of the possibility of contamination. The use of small pieces of cotton avoids both these difficulties.

In making measurements, one of these clean disks was placed in the chamber of the electroscope, in each case, before the natural drift was taken, to screen off any activity that might be in the chamber floor, as constant use of the instrument is liable to leave traces of active material on the bottom of the chamber. To reduce absorption of the radiations by the material to a negligible value, the films were made very thin, never containing over 0.2 mg. of material per square centimeter and in most cases less than this amount. Experiments showed that for thicker films there is a rapid falling off of activity with increase in weight.

The chamber of the electroscope used in all of these measurements was of such dimensions that the full range of the particles was utilized except for a negligible fraction. The activities were measured from time to time over a period of a year or more, and the activities, in divisions per minute, were computed on the basis of a gram of mineral in each case. A typical example: a 5.7-mg. film made from the tantalic oxide recovered from a ten-gram sample of carnotite gave a reading of 6.52 divisions per minute. Twenty milligrams of tantalic oxide had been previously added. The activity of all the protoactinium in the sample is $20/5.7 \times 6.52$ or 22.0 divisions per minute, and for one gram of the mineral the activity due to the protoactinium is 2.29 divisions per minute.

The initial activity due to the protoactinium in one gram of each of the minerals was obtained by plotting the activities, in divisions per minute, obtained as above, on the axis of ordinates, and the time, in days, on the axis of abscissas, and extending backward the growth curve to the axis of ordinates. The values obtained and their probable errors are given in Col. 4, Table I. The probable errors shown are based on at least six initial activities for each mineral.

To convert these initial activities due to the protoactinium in the different minerals, into atom for atom relations between protoactinium and uranium, it is necessary to know the α-ray activity of a gram of pure uranium, the percentage of uranium in the mineral and the a-ray activity due to the uranium in one gram of mineral.

In order to determine the α-ray activity of one gram of pure uranium, seven films of pure urano-uranic oxide, of the same dimensions as those above, were prepared and measured. The urano-uranic oxide used had been carefully freed from radioactivity by the method of McCoy.[11] The films varied in weight from 4.1 to 7.2 milligrams, and gave an average activity of 359.7 divisions per minute, per gram of oxide, or 423.9 divisions per minute, per gram of uranium element. The value 415.4 was obtained after deducting two per cent. due to the ionization of uranium X and uranium Y.[12] The average weight of the seven films was 4.9 milligrams, and since they had an area of 50.3 sq. cm., the average weight per square centimeter was approximately 1 X 10^{-4} grams. Johnstone and Boltwood[13] found that for films of approximately the same diameter as these, and weighing not more than ten milligrams, the absorption of the a-radiation was negligible. The probable error for the a-ray activities of the seven films was ±9.1 or about 2.2 per cent., when computed on the basis of one gram of uranium element.

The uranium content of the pitchblendes, soddite and carnotite were determined by the writer, using the emanation method. The value for the uranium content of thorianite was one made gravimetrically by Moore and Schlundt.[14]

Furthermore, the uranium content of the pitchblendes and soddite was very carefully determined, gravimetrically, by Mr. Fred Kavanagh, using the Randall[15] modification of the Boltwood[16] method for the determination of uranium in uranium minerals. The method used for the analysis of carnotite was that described in Bulletin 212, U. S. Bureau of Mines.[17] The value for carnotite was duplicated by an analysis made by Le Doux and Co.

The analytical results which follow give the percentage of uranium element in the different minerals.

Mineral	Emanation method	Gravimetric method
Carnotite, Colorado	20.43	18.65
Pitchblende, Bohemia	58.83	60.71
Pitchblende, Bohemia	62.22	62.98
Soddite, Belgian Congo	43.98	44.70
Thorianite, Ceylon	...	26.75

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[11] McCoy and Ashman, *Am. J. Sci.*, *26*, 521–530 (1909).

[12] Russell and Widdowson, *Phil.* Mag., 46, 920 (1923).

[13] Johnstone and Boltwood, *ibid.*, 40, 55 (1920).

[14] Unpublished results.

[15] Randall, *J. Am. Electrochem. Soc.*, *21*, 463497 (1912).

[16] Boltwood, *Phil. Mag.*, 9, 603 (1905).

[17] Bulletin 212, U. S. Bureau of Mines, pp. 225–226.

The gravimetric values given above were used in all the calculations. The a-ray activity, Col. **3**, Table I, due to the uranium in one gram of mineral was obtained in each case by multiplying the arbitrary constant 413.4 by the percentage of uranium in the mineral.

In order to reduce the measured protoactinium activities, Col. 4, Table I, to values corresponding to an equal number of uranium atoms, the protoactinium activities were multiplied by 61/72. This factor was determined as follows. According to Meyer and Schweidler[18] one α-particle from uranium I produces 1.16×10^5 pairs of ions in air over its entire range, and one a-particle from uranium II produces 1.27×10^5 pairs, the average being 1.22×10^5 pairs. One a-particle from protoactinium produces 1.44×10^5 pairs of ions in air over its entire range, hence the ionization due to the protoactinium is about fifteen per cent. greater atom for atom disintegrating than the average of that from uranium I and uranium II. To convert the protoactinium values to corresponding uranium values, they must be multiplied by the ratio $1.22 \times 10^5/1.44 \times 10^5$ or 61/72. These reduced values are given in Col. 5, Table I.

To illustrate the method of calculating the atom for atom relation, let us consider the sample of carnotite containing 18.65% of uranium element. The a-ray activity due to the uranium in one gram of the mineral is 415.4×0.1866 or 77.5 divisions per minute. The initial a-ray activity of the protoactinium in one gram of this mineral is 2.36 divisions per minute, and this times 61/72 equals 2.00 divisions per minute, which is the activity it would have if the a-particles from protoactinium had the same range as the average of those from uranium I and uranium II. Dividing 2.00 by 77.5 gives 0.0258, which is the ratio between the number of protoactinium atoms and atoms of uranium I and uranium II disintegrating in unit time. Multiplying 0.0258 by 2 gives 0.0516, or the ratio between the number of protoactinium atoms and atoms of uranium I or uranium II disintegrating. Multiplying 0.0516 by 100 gives 5.16, which is the number of atoms of protoactinium disintegrating per one hundred atoms of uranium I or uranium II. The values obtained for the different minerals are given in Col. 6, Table I.

TABLE I

VALUES FOR DIFFERENT MINERALS

Mineral	Uranium element, %	U activity per gram of mineral	Pa activity per gram of mineral	Pa activities reduced	Atoms of Pa per 100 atoms of U I and U II disintegrating
Carnotite, Colorado	18.65	77.5	2.36 ± 0.053	2.00	5.16
Pitchblende, Bohemia	60.71	252.2	4.16 ± .063	3.52	2.79
Pitchblende, Bohemia	62.98	261.6	2.26 ± .088	1.92	1.47
Soddite, Belgian Congo	44.70	185.7	4.03 ± .080	3.41	3.67
Thorianite, Ceylon	26.75	111.1	1.64 ± .031	1.39	2.50

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[18] Meyer and Schweidler, "Radioaktivitat," 1927, p. 629.

Discussion

It is seen that the ratio of protoactinium to uranium in the five minerals studied is by no means constant. The result is not entirely contradicted by the investigations of others, who have concluded that the ratio between protoactinium and uranium is constant in different minerals, for their experimental results show considerable variation in this ratio.

Largely on other evidence, many writers[19] of recent years have advocated the theory that the actinium series springs from an unknown isotope of uranium. The values they have variously assigned for the atomic weight of this isotope of uranium are 235, 237, 239 and 240.

The arguments in favor of an independent origin of the actinium series have centered around one or more of the following considerations: (1) the atomic weight of uranium being 238.18 has been taken as evidence of the existence of a higher isotope of uranium. However, this apparent excess weight of 0.18 has been explained on the basis of the "packing effect" by Plotnikow.[20] (2) There is no parallel to the formation of a branched series featuring a dual a-ray change. The other cases of branching, as in the "C" members of the uranium, thorium and actinium series, form one branch in an a-ray change and the other branch in a β-ray change. (3) The assumption of an independent origin of the actinium series seems to be more nearly in accord with the Geiger–Nuttall relation. (4) The discovery of certain rings in some pleochroic haloes can be explained on such an assumption.

Of all the suggested atomic weights for this independent source of the actinium series, the value 235 at present seems to be the most probable. Aston[21] found a faint line in the mass spectrum of some lead tetramethyl made from uranium lead obtained from Norwegian broggerite. He states that it cannot be due to lead as an impurity, because in ordinary lead 208 is about twice as strong as 207; neither can it be due to the products of radium or thorium. As he states, it is difficult to resist the conclusion that it is the end-product of the only other disintegration family, that of actinium.

Rutherford[22] likewise speculates regarding this isotope of lead, atomic weight 207, and concludes that it is highly probable that the mass 207 is mainly due to actinium lead and that the actinium series has its origin

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[19] Piccard, *Sci. Phys. Nat.*, [4] 44, 161–164 (1913); Soddy and Cranston, *Proc. Roy. Soc. London*, 94A, 385–404 (1917–1918); Adams, THIS JOURNAL, 42, 2205–2280 (1920); Joly, *Proc. Roy. Soc. London*, 102A, 682–704 (1923); Russell, *Phil. Mag.*, [6] 46, 642–656 (1923); Russell, *Nature*, 111, 703–704 (1923); 114, 717 (1924); 120, 545 (1927); Iimori and Yoshumura, *Int. Phys. Chem. Res. Tokyo*, 5, 12 (1926); Wilkins, *Phys. Rev.*, 29, 352 (1927).

[20] Plotnikow, *Z. Physik*, 28, 339–341 (1924).

[21] Aston, *Nature*, 123, 313 (1929).

[22] Rutherford, *ibid.*, 123, 313–314 (1929).

in an isotope of uranium which he calls "actino-uranium." He states that it is simplest to suppose that its mass is 235 and that it undergoes first an α- and then a β-ray transformation into protoactinium. The β-ray body is probably to be identified with uranium Y discovered by Antonoff.[23] On this view the successive transformations follow the order alpha, beta, alpha, beta, and differ in this respect from the main uranium series, which follows the order alpha, beta, beta, alpha. He states that it is possible for it to follow the uranium mode of disintegration, if it is assumed that the "actino-uranium" has an atomic weight of 239, atomic number 92 and disintegrates in an α-ray change followed by two β-rays. No evidence of such β-ray bodies has been found.

If it is true that 207 represents the mass of actinium lead, then it represents the first accurate determination of the atomic weight of a member of the actinium series and indicates that the atomic weight of protoactinium is 231. Thus it seems very probable that the origin of the actinium series is, as yet, an undiscovered isotope of uranium and the series is independent of the main uranium series. The results of this investigation lend support to this view.

Acknowledgments.—The writer wishes to express his sincere appreciation to Dr. Herman Schlundt, at whose suggestion this work was undertaken, for his personal interest and very helpful advice, throughout the investigation, and to Mr. Fred Kavanagh, whose very careful gravimetric determinations of the uranium content of some of the minerals added materially to the paper.

Summary

1. Since tantalum is the nearest homolog of protoactinium, extensive work was done on simplifying and standardizing a method which, with slight modifications, was used for the quantitative separation of tantalum from different uranium ores.

2. The uranium and protoactinium contents of five uranium ores from widely separated localities were determined and the atom for atom relation between uranium and protoactinium was computed in each case.

3. The results show that the protoactinium–uranium ratio in the different ores is far from constant, and consequently strengthens the view, now held by some, that the actinium series springs from a source other than uranium II.

COLUMBIA, *MISSOURI*

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[23] Antonoff, *Phil. Mag.*, **22**, 419 (1911).

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

EQUILIBRIA INVOLVING SOME COMPLEX IONS OF SILVER AND THE FREE ENERGY OF SOME SILVER COMPOUNDS[1]

BY MERLE RANDALL AND J. O. HALFORD

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Complex ions of silver are formed by the combination of silver ion with ammonia, cyanide, sulfite, thiosulfate, nitrite, thiocyanate, chloride, bromide, iodide and a few other substances. They fall into two classes: those formed from the ions of strong acids, including the halides and thiocyanates, in which case no one complex predominates, and those formed by the combination of silver ion with neutral, weakly basic, or weakly acidic substances in which only a single complex is predominantly present. The equilibria involving the latter class may be treated in a manner comparable to the treatment of simple ion equilibria. The latter class includes the ammonia and cyanide complexes, and it is with these that this paper is chiefly concerned.

When silver chloride is added to aqueous ammonia, silver ammonia complex is formed in accordance with the equation

$$\mathrm{AgCl(s)} + 2\mathrm{NH_4OH(aq.)} = \mathrm{Ag(NH_3)_2}^+ + \mathrm{Cl}^- + 2\mathrm{H_2O(l)} \qquad (1)$$

If we define K_m' by the equation[2]

$$K_m' = m(\mathrm{Ag(NH_3)_2}^+)m(\mathrm{Cl}^-)a^2\,(\mathrm{H_2O})/a^2\,(\mathrm{NH_4OH(aq.)}) \qquad (2)$$

it is obvious from the definition of the activity coefficient that the true equilibrium constant, K, is equal to $\gamma_\pm{}^2 K_m'$, where $\gamma_\pm$ is the activity coefficient of the complex salt. The activity of the water is included in the activity of the aqueous ammonia by definition and it will be found in the following article[3] that the activity coefficient of the ammonia in aqueous silver ammonia chloride is equal to the molality of the ammonia. If, then, we plot the logarithm of the reciprocal square root of K_m' against a function of the ionic strength, or its square root ($\mu^{1/2}$), the curve is similar to that obtained by plotting the logarithm of the activity coefficient (log $\gamma_\pm$) of a simple univalent salt against the same function of the ionic strength. The extrapolation to infinite dilution is made by superimposing our plot upon the similar plot for a suitable strong electrolyte.[2a] The logarithm of the reciprocal square root of K then coincides with the origin of the reference plot. From the value of log $(1/K^{1/2})$ and the measured values of

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[1] Abridged paper; original received December 22, 1927.

[2] The method of extrapolation is a modification of that adopted by (a) Randall and Vietti, THIS JOURNAL, 50, 1526 (1928). Reference to the present work was made by (b) Randall, Trans. *Faraday Soc.*, 23, 502 (1927). See also (c) Randall, *ibid.*, 23, 498 (1927); (d) Bray and MacKay, THIS JOURNAL, 32, 1207 (1910), and (e) Johnston, *ibid.*, 37, 2001 (1915), used similar equilibrium constants.

[3] Randall and Halford, *ibid.*, 52, 192 (1930).

log $(1/K_m'^{1/2})$ the activity coefficient of the complex salt may be obtained for a given ionic strength, for by definition

$$\log \gamma_{\pm} = \log (1/K_m'^{1/2}) - \log (1/K^{1/2}) \tag{3}$$

In a reaction in which the complex is formed by the addition of an ion as cyanide or sulfite, rather than by reaction with a neutral molecule as ammonia or hydrocyanic acid, another method of extrapolation must be employed. For example, in the reaction

$$AgI(s) + 2CN^- = Ag(CN)_2^- + I^-;\ K = a(Ag(CN)_2^-)a(I^-)/a^2(CN^-) \tag{4}$$

the value of K is probably not far different from the stoichiometrical equilibrium constant K_m; and if log K_m is plotted against the square root of the ionic strength, a straight line will be obtained if the activity coefficients of the cyanide complex and iodide ion are not far different from that of cyanide ion. In many cases K is obtained with sufficient accuracy by taking the numerical average of K_m.

The Solubility of Silver Chloride in Aqueous **Ammonia.**—$AgCl(s) + 2NH_4OH(aq.) = Ag(NH_3)_2^+ + Cl^- + 2H_2O(l)$.—Silver chloride was prepared by adding silver nitrate (0.5 M) to a slight excess of ammonium chloride (0.1 M) in the presence of very dilute nitric acid. After filtering and washing thoroughly, the precipitate was dried at 100°. At all times care was taken to avoid prolonged exposure to light. Aqueous ammonia was prepared by diluting U. S. P. ammonium hydroxide to the desired strength. The resulting solutions were found to be free from carbonate. Toluene was distilled before use, about 20% being discarded in the initial and final fractions.

Silver chloride, aqueous ammonia and toluene were placed in bottles with ground glass stoppers secured by small rubber caps and rotated in a thermostat at 25° for a period exceeding twenty-four hours. The mixtures were allowed to settle for several hours before analysis. To prevent loss of ammonia by evaporation, samples were forced by pressure from the reaction bottles through absorbent cotton filters into flasks containing a known weight of 0.1 M hydrochloric acid (standardized against sodium carbonate) in excess. The ammonia was extracted from the toluene by excess of standard acid, with methyl orange as the indicator since methyl red was found to dissolve in the toluene. The excess acid was titrated (methyl red, weight buret against sodium hydroxide). Samples for the determination of silver were received in excess of nitric acid and the silver was weighed as silver chloride.

The concentration of free ammonium hydroxide was calculated by subtracting twice the silver concentration plus the calculated ammonium ion from the total ammonia concentration (moles per 1000 g. of water in vacuum).

Experiments by Reychler[4] on the freezing points of solutions of the nitrate and sulfate of silver ammonia complex led to the formula $Ag(NH_3)_2^+$. Konowalow[5] and later Gaus,[6] from vapor pressure, and Berthelot and Delépine,[7] from the heat effects attending the addition of silver nitrate in excess to aqueous ammonia and of aqueous ammonia in excess to silver nitrate, obtained the same formula. The work of Whitney and Mel-

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[4] Reychler, *Ber.*, 28, 555 (1895).

[5] Konowalow, Z. *physik. Chem.*, 28,558 (1898).

[6] Gaus, *Z. anorg. Chem.*, 25,236 (1900).

[7] Berthelot and Delépine, *Compt. rend.*, 129,326 (1899).

cher,[8] which included transference, freezing point and conductivity experiments, led to a similar result. More recently, de Wijs[9] has presented evidence that in saturated solutions of the base $Ag(NH_3)_2OH$ the average number of ammonia molecules per silver molecule is slightly greater than two. Our experiments with silver chloride solutions, in which the ratio of free ammonia is high in comparison to the complex ion concentration, suggest the presence of small amounts of the higher forms, but at present we are unable to present definite evidence as to the constitution of the complex. Our treatment is independent of the existence of small amounts of the higher forms.

The results of our measurements are given in Table I. Cols. 1 and 2 give the total molality of ammonia and silver constituents, Cols. 3 and 4 the molality of ammonium ion and of undissociated ammonium hydroxide as calculated[10] by the method of approximations, on the basis that the formula of the complex ion is $Ag(NH_3)_2^+$, and Cols. 5 and 6 the functions log $(1/K_m'^{1/2})$ and $\mu^{1/2}$.

TABLE I

SOLUBILITY OF SILVER CHLORIDE IN AQUEOUS AMMONIA AT 25°

Total $m(NH_3)$	Total $m(Ag)$	Calcd. $m(NH_4^+)$	Calcd. $m(NH_4OH)$	Log $(1/K_m'^{1/2})$	$\mu^{1/2}$
0.1089	0.005665	0.0015	0.0960	1.229	0.0835
1.3039	.0895	.0051	1.1198	1.097	.307
1.710	.1256	.0065	1.4525	1.063	.363
1.8782	.1379	.0068	1.5956	1,064	.380
2.1339	.1628	.0074	1.8009	1.054	.413
2.6400	.2151	.0085	2.2014	1.010	.473
2.9091	.2395	.0090	2.4211	1.005	.498

The values of log $(1/K_m'^{1/2})$ are plotted in Fig. 1 against the square root of the ionic strength. We also show the values of this constant as calculated from the data of other authors.[11]

By superimposition of the plot of Pig. 1 upon the standard activity coefficient curve,[2a] we find that the activity coefficient of the aqueous silver ammonia chloride is slightly less than that given by the limiting curve[2a]

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[8] Whitney and Melcher, THIS JOURNAL, **23,** 68 **(1903).**

[9] De Wijs, "Thesis," Delft, **1923.**

[10] $NH_4OH(aq.) = NH_4^+ + OH^-$; $K_{298 \cdot 1} = 18.1 \times 10^{-6}$ [Noyes and Kanolt, *Publ. Carnegie Inst.*, Washington, D. C., No. **63, 285** (1907)]. The activity coefficient in the mixture was taken as that of sodium hydroxide [see Randall and Failey, *Chem. Rwiews,* 4, **291** (1927)].

[11] (a) Bodlander and Fittig, *Z. physik. Chem.*, **39, 597 (1901);** (b) Straub, *ibid.*, 77, **332 (1911);** (c) Whitney and Melcher, **Ref. 8.** The values given by Whitney and Melcher are in concentration units. More weight should be given to their values in the dilute solutions as the data for converting concentrations to molalities is not known. (d) The data and calculations are given by Randall in the section on Free Energy, "International Critical Tables," Vol. VII, McGraw-Hill Book Co., New York, **1930.**

of the Debye–Hückel equation. We take $\log (1/K'^{1/2})$ equal to 1.272 ± 0.002, hence

$$AgCl(s) + 2NH_4OH(aq.) = Ag(NH_3)_2^+ + Cl^- + 2H_2O(l);\ K_{298.1} = 2.858 \times 10^{-3};\ \Delta F^\circ_{298.1} = 3472 \text{ cal.} \quad (5)$$

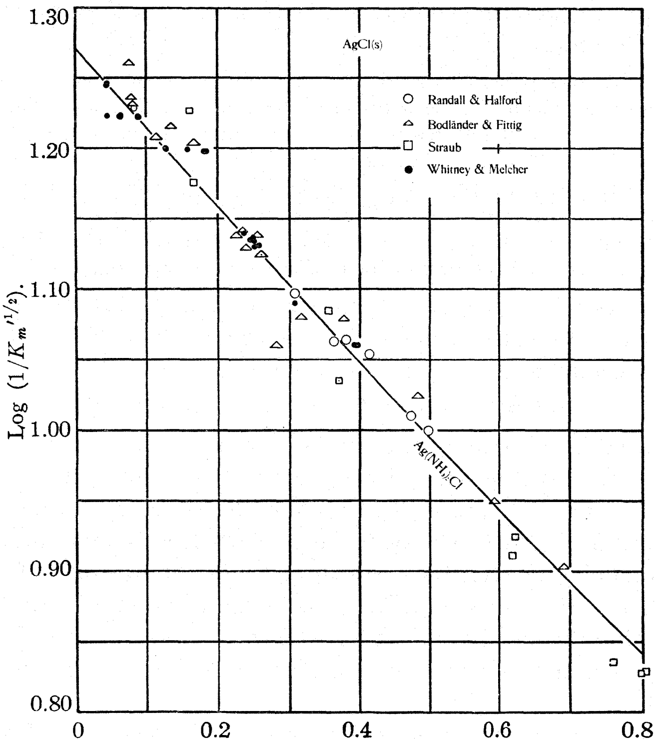
The values of the logarithm of activity coefficient of the silver ammonia chloride at round molalities are given in Table II.

Table II

Activity Coefficient of Silver Ammonia Chloride

m	0.001	0.002	0.005	0.01	0.02	0.05	0.1	0.2	0.5
Log γ	−0.017	−0.024	−0.040	−0.056	−0.080	−0.126	−0.176	−0.248	−0.382

The Solubility of Silver Oxide in Aqueous Ammonia.—$^1/_2Ag_2O(s) + 2NH_4OH(aq.) = Ag(NH_3)_2^+ + OH^- + {^3/_2}H_2O(l)$. In this reaction



Square root of ionic strength.

Fig. 1.—Solubility of silver chloride in aqueous ammonium hydroxide at 25°.

the values of K_m' calculated from the distribution ratios of ammonia between toluene and water do not correct completely for the activity of the water since the reaction of two moles of ammonia produces only 1.5 moles of water. The reciprocal square root of the equilibrium constant is given by

$$1/K^{1/2} = a(\mathrm{NH_4OH(aq.)})/[a(\mathrm{Ag(NH_3)_2}^+)a(\mathrm{OH})^-a^{3/2}(\mathrm{H_2O})]^{1/2} \qquad (6)$$

Since by definition

$$a(\mathrm{NH_4OH(aq.)}) = \gamma' m(\mathrm{NH_4OH})a(\mathrm{H_2O}) \qquad (7)$$

then

$$1/K_m'^{1/2} = \gamma' m(\mathrm{NH_4OH})a^{1/4}(\mathrm{H_2O})/m(\mathrm{Ag(NH_3)_2}^+)m(\mathrm{OH})^- \qquad (8)$$

The activity of the water is involved in Equation 8 only as the fourth root. In our measurements the activity of the water does not differ from unity by more than 10% at the highest concentration investigated. Therefore, if we include the fourth root of the activity coefficient of the water in that of the complex base, the maximum error introduced is 2.5% and this only at the highest concentrations. The equilibrium at ionic strengths, 0.01 to 0.27, was determined in the same manner as in the case of the silver ammonia chloride.

Silver oxide was prepared by adding 0.5 N silver nitrate to an excess of 0.1 N barium hydroxide which had been found to be free from halides. The precipitate was washed thoroughly and heated to boiling in distilled water to decompose any silver carbonate. This method of preparation did not exclude small quantities of barium carbonate but the presence of that substance should have no effect on the measurements.

The silver was determined by the method of Volhard. In a few cases the equilibrium was approached from supersaturation by diluting mixtures which had already come to equilibrium and rotating for more than twenty-four hours in the thermostat.

In the more dilute solutions, the distribution experiments were omitted because of the difficulty of measuring accurately the concentration of ammonia in the toluene layer. The average value[3]

$$\mathrm{NH_4OH(aq.\ in\ Ag(NH_3)_2OH)};\ (\log \gamma')/\mu = 0.136 \qquad (9)$$

has been used in calculating the values of $1/K_m'^{1/2}$ from those of $1/K_m^{1/2}$.

The results of our measurements are given in Table III. Col. 1 gives molality of the total base, Col. 2 that of the silver constituent which is also the ionic strength, Col. 3 the molality of the free ammonium hydroxide, equal to molality of total base less three times the molality of silver constituent, Col. 4 the value of $1/K_m^{1/2}$, Col. 5 the value of the same function after changing the molality of the NH_4OH to activity by means of Equation 9, and Cols. 6 and 7 have the same significance as the corresponding columns in Table I.

The values of Col. 6 are plotted against $\mu^{1/2}$ in Fig. 2. This plot also shows the values of $\log(1/K_c'^{1/2})$ calculated from the results of similar measurements (moles per liter) by Whitney and Melcher.[8,11c,d] Olmer[12] also studied this reaction at room temperature, and at ionic strengths from 0.1 to 1.4. His results are qualitatively in agreement with those of Fig. 2 and show that the activity coefficient of the silver ammonia hydroxide

[12] Olmer, Bull. *soc. chim.*, **35, 333 (1924).**

rapidly increases in the more concentrated solutions, thus offering additional evidence that this substance is a strong base.

TABLE III

SOLUBILITY OF SILVER OXIDE IN AQUEOUS AMMONIA AT 25°

Total m base	$m(Ag(NH_3)_2^+)$	$m(NH_4OH)$	$1/K_m^{1/2}$	$1/K_m'^{1/2}$	Log $(1/K_m'^{1/2})$	$\mu^{1/2}$
0.05302	0.01155	0.01838	1.59	1.59	0.201	0.107
.05532	.01282	.01667	1.32	1.32	.119	.113
.05821	.01338	.01806	1.35	1.36	.133	.116
.06173	.01406	.01955	1.39	1.40	.146	.119
.1479	.03499	.04289	1.23	1.25	.097	.187
.1575	.03606	.04932	1.37	1.39	.143	.190
.2456	.05787	.07198	1.25	1.26	.100	.240
.3155	.07352	.09490	1.29	1.32	.120	.272
.3200	.07535	.09494	1.26	1.29	.111	.274
.3540	.07787	.1231	1.55	1.59	.201	.279
.6519	.1525	.1945	1.28	1.34	.127	.391
.6767	.1582	.2021	1.28	1.34	.127	.398
.6950	.1623	.2082	1.28	1.35	.130	.403
.8673	.2033	.2574	1.26	1.34	.127	.452
.9518	.2225	.2841	1.26	1.35	.130	.472
1.2304	.2888	.3642	1.26	1.38	.140	.538

Noyes and Kohr and later Newton[13] have determined the ratio of potassium chloride and potassium hydroxide shaken with an excess of silver

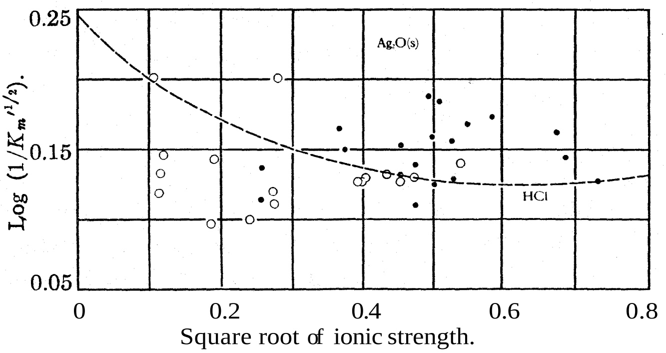


Fig. 2.—Solubility of silver oxide in aqueous ammonium hydroxide at 25°.

oxide and silver chloride. When their values of K_c and K_m are plotted against $\mu^{1/2}$ they appear to be in agreement. An extrapolation to $\mu^{1/2} = 0$ gives

$$AgCl(s) + OH^- = {}^1/_2Ag_2O(s) + Cl^-;\ \log K_{298.1} = -2.050 \pm 0.003;$$
$$\Delta F^\circ_{298.1} = 2798 \pm 5 \text{ cal.} \quad (10)$$

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[13] (a) Noyes and Kohr, Z. *physik.* Chem., 42,336 (1902); (b) Newton, THIS JOURNAL, 50,3258 (1928).

and this value gives a reasonable ratio between the activity coefficients of $OH-$ and Cl^- in the more concentrated solutions.[14]

Combining Equations 5 and 10 we find

$$^1/_2Ag_2O(s) + 2NH_4OH(aq.) = Ag(NH_3)_2^+ + OH^- + ^3/_2H_2O(l); \log K_{298\cdot 1} = -0.494 \pm 0.005; \quad \Delta F^\circ_{298\cdot 1} = 674 \text{ cal.} \quad (11)$$

whence we find log $(1/K^{1/2}) = 0.247$ and this point is shown on Fig. 2 as the intersection of the dotted curve with the ordinate $\mu^{1/2} = 0$. The dotted curve is that of the logarithm of activity coefficient of hydrochloric acid plus 0.247. In general, the activity coefficient of strong bases is slightly less than that of hydrochloric acid. Our results show agreement with the assumption that the complex hydroxide is an approximately normal strong base in the region of $\mu^{1/2}$ = about 0.4. If we were to attempt to superimpose Fig. 2 upon the plot of log γ for strong bases so as to pass through the points at about $\mu^{1/2} = 0.2$, then we should find the activity coefficient of silver ammonia hydroxide much higher than that of any other substance at 0.2 M, and we should need to explain a discrepancy between the free energy as given by Equation 10 and the difference between Equations 5 and 11. A possible explanation of the anomalous activity coefficient of the hydroxide of silver ammonia complex is a change in the fineness of subdivision of the solid phase with the concentration and nature of the electrolyte. The probable analytical errors are not of the right sign to explain the unusual results.

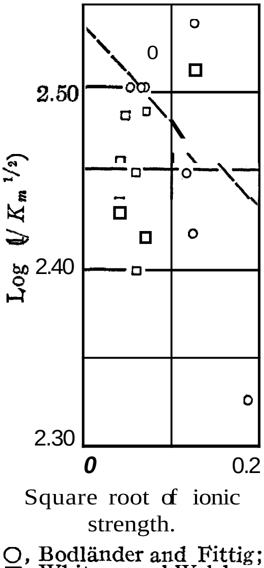

Fig. 3.—Solubility of silver bromide in aqueous ammonia.

$AgBr(s) + 2NH_4OH(aq.) = Ag(NH_3)^+ + Br^- + 2H_2O(l)$.—We show in Pig. 3 the values of log $(1/K_m'^{1/2})$ and log $(1/K_c'^{1/2})$ as calculated from the measurements of Bodländer and Fittig[11a,d] and of Whitney and Melcher[8,11c,d] plotted against $\mu^{1/2}$ or $\mu_c^{1/2}$. Account was taken of the amount of NH_4^+ present. The limiting value, log $(1/K^{1/2})$, was calculated from Equation 5 and the free energies of silver chloride, silver bromide, chloride and bromide ions,[15] and found to be 2.537. The experimental values are found to be in agreement with this value, and show that the activity coefficient of silver ammonia bromide is somewhat lower than that of the complex chloride. We thus write

$$AgBr(s) + 2NH_4OH(aq.) = Ag(NH_3)_2^+ + Br^- + 2H_2O(l); \log K_{298\cdot 1} = -5.074 \pm 0.005; \quad \Delta F^\circ_{298\cdot 1} = 6926 \text{ cal.} \quad (12)$$

Solubility **of** Silver Cyanide in **Hydrocyanic Acid.** $AgCN(s) + HCN(aq.) = H^+ + Ag(CN)_2^-$.—We have studied this reaction in solutions of

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[14] *See* Randall and Breckenridge, THIS JOURNAL, 49, 1435 (1927).

[15] Randall and Spencer, unpublished calculations.

hydrocyanic acid from 0.1 to 0.5 *M*. When silver cyanide is allowed to come to equilibrium with aqueous hydrogen cyanide, a small concentration of a strong acid is produced. A measurement of this acid concentration and the concentration of hydrocyanic acid permits the calculation of the equilibrium constant. The fugacity of the hydrogen cyanide is proportional to its molality.[3]

Hydrocyanic acid was prepared by the method used by Perry and Porter,[16] who investigated the vapor pressures of solid and liquid hydrogen cyanide. A solution of 18 N sulfuric acid was added slowly to powdered potassium cyanide in a distilling flask and the vapors were collected in water. The production of cyanogen by oxidation is not probable because of the slow rate of oxidation exhibited by sulfuric acid of the strength used. Perry and Porter had no difficulty with the cyanogen impurity. Silver cyanide was precipitated in dilute solution by the addition of silver nitrate to a slight excess of potassium cyanide. Some of the experiments were carried out in glass stoppered bottles, others in sealed flasks.'' In a few cases equilibrium was approached from supersaturation by maintaining the mixtures at a temperature of about 35" for several hours before rotating in the thermostat. The mixtures of silver cyanide, benzene and aqueous hydrocyanic acid were rotated in the thermostat at 25° for several days. To prevent loss of hydrogen cyanide by evaporation, samples were forced by pressure from the reaction bottles. The acid concentration was determined by titration with 0 01 N sodium hydroxide. Samples for the determination of cyanide were received in excess of sodium hydroxide and titrated by the method of Liebig to an endpoint with potassium iodide.

In Table IV we have summarized the results of the solubility measurements. Column 1 gives the molality of hydrocyanic acid, Col. 2 that of the complex acid, Col. 3 the reciprocal square root of the stoichiometrical constant, Col. 4 its logarithm and Col. 5 the square root of the ionic strength. The acid concentration produced in these equilibria is so small that an accurate determination of the equilibrium constant is difficult. We have plotted, in Fig. 4, $1/K_m^{1/2}$ against the sauare root of the ionic strength and for the purpose of making the very slight extrapolation to zero molality have taken the point determined by the mean value of $1/K_m^{1/2}$ and the mean value of . From this point we have extrapolated to zero ionic strength with the aid of the curve for hydrochloric acid and have obtained for log $(1/K^{1/2})$ the value 2.212.

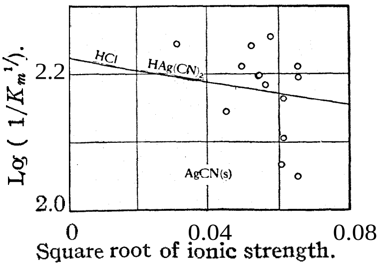

Fig. 4.—Solubility of silver cyanide in aqueous hydrogen cyanide at 25°.

$$AgCN(s) + HCN(aq.) = H^+ + Ag(CN)_2^-;\ K_{298.1} = 3.77 \times 10^{-5};\ \Delta F^\circ_{298.1} = 6038 \text{ cal.} \quad (13)$$

Solubility of Silver Chloride in Hydrocyanic Acid. $AgCl(s) + 2HCN(aq.) = 2H^+ + Ag(CN)_2^- + Cl^-$.—The solubility of silver chloride in

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[16] Perry and Porter, THIS JOURNAL, 48,299 (1926).

TABLE IV

SOLUBILITY OF SILVER CYANIDE IN AQUEOUS HYDROCYANIC ACID AT 25°

m(HCN(aq.))	m(HAg(CN)$_2$)	Log $(1/K_m^{1/2})$	$\mu^{1/2}$	m(HCN(aq.))	m(HAg(CN)$_2$)	Log $(1/K_m^{1/2})$	$\mu^{1/2}$
0.0296	0.000983	2.244	0.0314	0.2275	0.00424	2.050	0.0652
.1016	.000204	2.144	.0452	.2325	.00316	2.184	.0562
.1596	.00245	2.211	.0496	.3000	.00375	2.164	.0612
.1780	.00366	2.067	.0606	.3625	.00331	2.254	.0576
.1825	.00246	2.198	.0544	.4230	.00400	2.210	.0653
.2124	.00292	2.197	.0541	.4260	.00511	2.106	.0612
.2245	.00272	2.241	.0523	.4465	.00427	2.195	.0654

aqueous hydrocyanic acid has been treated in the same manner as that of silver cyanide.

Our analysis determines only the molality of the strong acid and the molality of the hydrocyanic acid. In the simplest interpretation the complex cyanide and the chloride would have the same molality equal to half that of the acid. From the equilibrium constant of the solubility of silver cyanide in aqueous hydrogen cyanide, it is evident that if in our solutions the complex ion concentration were half that of the acid, the solutions would be supersaturated with respect to silver cyanide. Therefore, we must introduce a correction to account for the reaction

$$\mathrm{AgCl(s)} + \mathrm{HCN(aq.)} = \mathrm{AgCN(s)} + \mathrm{H^+} + \mathrm{Cl^-} \qquad (14)$$

The chloride ion concentration is greater than that of the silver cyanide complex.

Columns 1 to 4 of Table V give the molality of the hydrogen cyanide, the hydrogen ion, the complex and of the chloride, Col. 5 the reciprocal fourth root of K_m, Col. 6 its logarithm and the last the square root of the ionic strength. To determine the equilibrium constant we have plotted log $(1/K_m^{1/4})$ against the square root of the ionic strength and have extrapolated to zero ionic strength with the aid of the curve for hydrochloric acid. This gives us log $K_m^{-0.25} = 2.180$ and

$$\mathrm{AgCl(s)} + \mathrm{2HCN(aq.)} = \mathrm{Ag(CN)_2^-} + \mathrm{2H^+} + \mathrm{Cl^-};\ K_{298.1} = 1.9 \times 10^{-9};\ \Delta F^\circ_{298.1} = 11{,}902\ \mathrm{cal.} \qquad (15)$$

TABLE V

SOLUBILITY OF SILVER CHLORIDE IN AQUEOUS HYDROCYANIC ACID AT 25°

m(HCN(aq.))	m(Acid)	m(Complex)	m(Chloride)	Log $(1/K_m^{1/4})$	$\mu^{1/2}$
0.0938	0.00303	0.00132	0.00161	2.163	0.0552
.1831	.00430	.00182	.00258	2.146	.0652
.2292	.00493	.00199	.00294	2.141	.0702

Solubility of Silver Iodide in Potassium Cyanide. $\mathrm{AgI(s)} + \mathrm{2CN^-} = \mathrm{Ag(CN)_2^-} + \mathrm{I^-}$.—Measurements were made with "precipitated" silver iodide and also with a crystalline form. The precipitated silver iodide was prepared by adding 0.5 N silver nitrate to an excess of 0.1 *N* potassium iodide. The precipitate was separated and dried at 100°. The preparation of hexagonal crystals of silver iodide involved a digestion of mercuric iodide with 0.1 M silver nitrate at the boiling point. This method does not exclude mercury salts but these should have no effect on the reaction other than to cause a slight increase of ionic strength,

The silver iodide was rotated in a thermostat in contact with a potassium cyanide solution of known strength for several days. Sufficient sodium hydroxide was added to repress the hydrolysis of the cyanide. To determine the silver content a sample was acidified with nitric acid and heated to remove hydrogen cyanide; this precipitated the silver iodide, which was collected on a filter, dried at 100° and weighed.

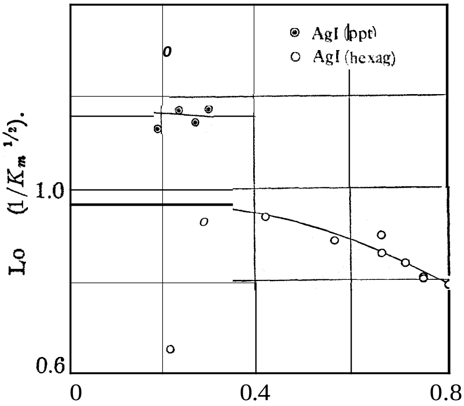

Fig. 5.—Solubility of silver iodide in aqueous potassium cyanide at 25°.

The measurements of the solubility of the precipitated and crystalline forms are summarized in Tables VI and VII and the results are plotted in Fig. 5. The limiting value of log $K^{1/2}$ in the case of precipitated silver iodide was calculated by combining Equation 15 with the free energy of ionization of aqueous hydrogen cyanide[17] and the standard free energies of the silver chloride[18] and silver iodide electrodes.[15] We thus find

$$AgI(ppt.) + 2CN^- = Ag(CN)_2^- + I^-;\ K_{298.1} = 221;\ \Delta F°_{298.1} = -3201 \text{ cal.} \quad (16)$$

The greatest uncertainty is in the value for the free energy of ionization of the hydrogen cyanide. The value of log $K^{1/2} = 1.172$ is shown in Fig. 5 as the limit of the extrapolated curve. This extrapolation appears to be reasonable. In the extrapolation of the curve for the hexagonal silver iodide, it was made parallel to the curve for the precipitated variety, whence log $K^{1/2} = 0.978$, and

$$AgI(hexag.) + 2CN^- = Ag(CN)_2^- + I^-;\ K_{298.1} = 90.4;\ \Delta F°_{298.1} = -2670 \text{ cal.} \quad (17)$$

From the difference of Equations 16 and 17

$$AgI(ppt.) = AgI(hexag.);\ \Delta F°_{298.1} = -531 \text{ cal.} \quad (18)$$

TABLE VI

SOLUBILITY OF PRECIPITATED SILVER IODIDE IN POTASSIUM CYANIDE AT 25°

Total $m(CN^-)$	m(AgI)	m(CN^-(free))	m(NaOH (added))	Log ($K_m{}^{1/2}$)	$\mu^{1/2}$
0.01837	0.00866	0.00065	0.0197	1.131	0.192
.03676	.01778	.00120	.0200	1.170	.238
.05521	.02666	.00191	.0199	1.146	.275
.07337	.03549	.00239	.0196	1.173	.305

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

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

TABLE VII

SOLUBILITY OF HEXAGONAL SILVER IODIDE IN POTASSIUM CYANIDE AT 25°

Total-m(CN)	m(AgI)	m(CN$^-$(free))	m(NaOH (added))	Log ($K_m^{1/2}$)	$\mu^{1/2}$
0.0208	0.0102	0.00049	0.0244	1.301	0.212
.0208	.0093	.0021	.0244	.653	.212
.0405	.0191	.00224	.0444	.931	.292
.0836	.0386	.00456	.0946	.938	.423
.0836	.0396	.00434	.0946	.961	.423
.146	.0684	.00889	.1738	.886	.566
.195	.0911	.0126	.2433	.858	.663
.195	.0916	.0116	.2433	.897	.663
.261	.1217	.0177	.2448	.836	.712
.318	.1474	.0232	.2421	.802	.748
.318	.1475	.0230	.2421	.806	.748
.398	.1840	.0300	.2424	.788	.800

Solubility of Silver Thiocyanate, Silver Iodide and Silver Bromide in Potassium **Thiocyanate.**—Bodländer and Fittig[11a] have given the formula and free energy of the silver thiocyanate complex. Their data suggested that the free energies of silver bromide and silver iodide might be linked through their solubility in potassium thiocyanate. We have measured the solubility of silver thiocyanate, silver bromide and silver iodide in solutions of potassium thiocyanate.

Silver bromide was made by precipitating potassium bromide in dilute solution with silver nitrate in the presence of dilute nitric acid; silver thiocyanate was prepared in an analogous manner. Potassium thiccyanate of known strength was rotated in bottles in the thermostat in contact with the solid phase at 25° for several days. The silver content of the sample selected for analysis was determined gravimetrically by precipitating the dissolved solid and weighing. The thiocyanate was oxidized by heating with 2 N nitric acid, the solid precipitating during the oxidation. When the solid phase was silver thiocyanate, a small concentration of potassium thiocyanate was added to the solution before filtering to replace any silver thiocyanate which had been oxidized.

In the silver bromide equilibria agreement was obtained in two sets of experiments in which rotation was continued respectively for two days and three weeks. This eliminates the time factor in the explanation of the results. In the silver thiocyanate equilibria a few rough measurements were made in which the equilibrium was approached from supersaturation. They were consistent with the others.

Table VIII gives the results of the solubilities of silver bromide. The first column gives the total molality of potassium thiocyanate, the second of the dissolved silver bromide, the third the free thiocyanate if the formula of the complex is $Ag(CNS)_2^-$, and the fourth a function of the equilibrium constant.

Table IX gives similar results for the solubility of precipitated silver iodide in potassium thiocyanate, while Table X summarizes the silver thiocyanate equilibria.

TABLE VIII

SOLUBILITY OF SILVER BROMIDE IN POTASSIUM THIOCYANATE AT 25°

$AgBr(s) + 2CNS^- = Ag(CNS)_2^- + Br^-$

Total m(KCNS)	m(AgBr)	m(KCNS (free))	Log ($K_m{}^{1/2}$)
0.2510	0.0011	0.249	−2.340
.2702	.0012	.267	−2.340
.5205	.0095	.501	−1.722
.5819	.0085	.564	−1.824
.7577	.0285	.701	−1.390
.7762	.0307	.715	−1.367
1.0089	.0663	.875	−1.122
1.0089	.0668	.875	−1.118

TABLE IX

SOLUBILITY OF PRECIPITATED SILVER IODIDE IN POTASSIUM THIOCYANATE AT 25°

$AgI(amorp.) + 2CNS^- = Ag(CNS)_2^- + I^-$

Total m(KCNS)	$m \times 10^4$ (AgI)	m(KCNS (free))	Log ($K_m{}^{1/2}$)
0.202	0.20	0.202	−4.00
.315	.14	3 1	−4.30
.425	.67	.425	−3.91
.500	.51	.500	−4.00
.608	.40	.608	−4.18
.710	.97	.710	−3.85
.765	1.46	.765	−3.72
1.009	1.63	1.008	−3.80

TABLE X

SOLUBILITY OF SILVER THIOCYANATE IN POTASSIUM THIOCYANATE AT 25°

$AgCNS(s) + CNS^- = Ag(CNS)_2^-$

Original m(KCNS)	m(AgCNS)	m(KCNS(free))	Log (K_m)
0.312	0.00202	0.310	−2.187
.564	.0121	.512	−1.627
.870	.0458	.824	−1.255
1.124	.0985	1.026	−1.018

Evidently we cannot account for the solubility of these solids in potassium thiocyanate by the formation of a single complex ion $Ag(CNS)_2^-$. Attempts to interpret these results by other simple assumptions have been unsuccessful. The reactions here studied are analogous to those of the silver halides in halide ion solutions. By assuming a sufficient number of complexes, and determining the equilibrium constants among these by the method of approximations, one should be able to satisfy the experimental data, but it is doubtful if such a calculation would be of more than academic interest.

The Solubility of Silver Chloride in Sulfite Solutions.—From the measurements of Luther and Leubner,[19] the details of which are found in another place,[11d] we find on extrapolation to infinite dilution

$$AgCl(s) + 2SO_3^{--} = Ag(SO_3)_2^{---} + Cl^-; K_{298.1} = 0.0578; \Delta F^\circ_{298.1} = 1690 \text{ cal.} \quad (19)$$

The Solubility of Silver Bromide in Sulfite Solutions.—Likewise from the solubility measurements of Luther and Leubner,[11d,19] we find on extrap-

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[19] **Luther** and Leubner, Z. anorg. *Chem.*, 74, 393 (1911).

olating to zero ionic strength along a line parallel to the curve of log K_c against $\mu_c^{1/2}$ for Reaction 19, the value log K = 3.754, whence

$$AgBr(s) + 2SO_3^{--} = Ag(SO_3)_2^{---} + Br^-;\ K_{298\cdot1} = 1.76 \times 10^{-4};\ \Delta F^\circ_{298\cdot1} = 5124\text{ cal.} \quad (20)$$

The difference in the values of the free energy from Equations 19 and 20 is —3434 cal. while the corresponding difference between Equations 5 and 12 is −3454 cal. which is a very satisfactory check upon the accuracy of the measurements and the assumptions made in the various extrapolations.

The Equilibrium of Silver Chloride and Silver Bromide with Silver **Thiocyanate.**—From the measurements of Hill,[20,11d] we find by extrapolation

$$AgCl(s) + CNS^- = AgCNS(s) + Cl^-;\ K_{298\cdot1} = 161;\ \Delta F^\circ_{298\cdot1} = -3012\text{ cal.} \quad (21)$$

$$AgBr(s) + CNS^- = AgCNS(s) + Br^-;\ K_{298\cdot1} = 0.505;\ \Delta F^\circ_{298\cdot1} = 404\text{ cal.} \quad (22)$$

The difference between Equations 21 and 22 is —3416 cal., which is also in satisfactory agreement with the difference between Equations 5 and 12.

The Free Energy of Some Silver Complexes

Silver Ammonia Complex.—The free energy of the silver ammonia complex ion is best calculated from Equation 5, which is based upon the solubility of silver chloride. We have already shown that the results based upon the solubility of silver oxide (Equation 11) and of silver bromide (Equation 12) in aqueous ammonia are in agreement with Equation 5. Hence combining with the values for the free energy of formation of silver chloride,[15] aqueous ammonia,[11d,17] chloride ion,[18] and liquid water,[11d,17] we find

$$Ag(s) + N_2(g) + 3H_2(g) = Ag(NH_3)_2^+ + E^-;\ \Delta F^\circ_{298\cdot1} = -4003\text{ cal.} \quad (23)$$

Dissociation Constant of Silver Ammonia Complex.—By combination of Equation 23 with the free energy of silver ion,[11d,17] liquid water and ammonia we find

$$Ag(NH_3)_2^+ + 2H_2O(l) = Ag^+ + 2NH_4OH(aq.);\ \Delta F^\circ_{298\cdot1} = 9851\text{ cal.};\ K_{298\cdot1} = 7.86 \times 10^{-8} \quad (24)$$

Silver Cyanide Complex.—We calculate the free energy of formation of silver cyanide complex from Equation 15 and the free energies of silver chloride,[15] aqueous hydrogen cyanide[11d,17] (27,510) and chloride ion,[18] whence

$$Ag(s) + 2C(graph.) + N_2(g) + E^- = Ag(CN)_2^-;\ \Delta F^\circ_{298\cdot1} = 72{,}047\text{ cal.} \quad (25)$$

As in the case of the silver ammonia complex, this value has already been shown to be in agreement with that calculated from other reactions. (Equation 16.)

Silver Cyanide.—From Equations **13** and *25* with the free energy of aqueous hydrogen cyanide we find for the free energy of formation of silver cyanide.

$$Ag(s) + C(graph.) + \tfrac{1}{2}N_2(g) = AgCN(s);\ \Delta F^\circ_{298\cdot1} = 38{,}499\text{ cal.} \quad (26)$$

Dissociation Constant of **Silver Cyandie** Complex.—Prom Equation

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[20] Hill, THIS JOURNAL, 30, 68 (1908).

15, the free energy of chloride ion, silver chloride and the free energy of dissociation of aqueous hydrogen cyanide,[11d,17] we find

$$Ag(CN)_2^- = Ag^+ + 2CN^-;\ \Delta F^\circ_{298.1} = 25{,}141\ \text{cal.};\ K_{298.1} = 3.81 \times 10^{-19} \quad (27)$$

Solubility Product of Silver Cyanide.—From Equations 13 and 27 we find

$$AgCN(s) = Ag^+ + CN^-;\ \Delta F^\circ_{298.1} = 19{,}319\ \text{cal.};\ K_{298.1} = 7 \times 10^{-15} \quad (28)$$

Hydrogen Silver Cyanide.—Since the results of Table IV and Fig. 4 show the hydrogen silver cyanide to be a strong acid, we may write from Equation 25

$$Ag(s) + 2C(\text{graph.}) + N_2(g) + {}^1/_2H_2(g) = HAg(CN)_2;\ \Delta F^\circ_{298.1} = 72{,}047\ \text{cal.} \quad (29)$$

Silver Sulfite Complex.—From Equation 19 and the free energy of silver chloride,[15] chloride ion[18] and sulfite ion,[11d,17] we find

$$Ag(s) + 2S(\text{rhomb.}) + 3O_2(g) + 3E^- = Ag(SO_3)_2^{---};\ \Delta F^\circ_{298.1} = -226{,}545\ \text{cal.} \quad (30)$$

We may consider this result verified by Equation 20. The largest uncertainty in the value lies in the uncertainty in the free energy of sulfite ion.

Dissociation Constant of Silver Sulfite Complex.—From Equation 30 and the free energies of silver and sulfite ion,[11d,17] we find

$$Ag(SO_3)_2^{---} = Ag^+ + 2SO_3^{--};\ \Delta F^\circ_{298.1} = 11{,}633\ \text{cal.};\ K_{298.1} = 3.00 \times 10^{-9} \quad (31)$$

Summary

A method has been presented for the treatment of equilibria involving the solution of difficultly soluble compounds in weak acids or bases to form complex ions. The method has been applied to new data for the solubility of silver chloride and silver oxide in ammonium hydroxide and of silver chloride and silver cyanide in aqueous hydrogen cyanide.

The solubility of precipitated and crystalline silver iodide in potassium cyanide, and the solubility of silver bromide, silver iodide and silver thiocyanate in potassium thiocyanate has been determined.

The activity coefficient of silver ammonia chloride, of silver ammonia bromide, of silver ammonia hydroxide and of complex silver cyanide acid has been determined.

The data for the solubility of silver salts in weak acids have been reviewed and the free energy of several complex ions calculated.

The data for the free energy of several silver salts have been considered and the free energies of some of the silver compounds are presented in the following table.

TABLE XI

FREE ENERGY OF SOME SILVER COMPOUNDS

Substance	$\Delta F^\circ_{298.1}$, cal.	Equation	Substance	$\Delta F^\circ_{298.1}$, cal.	Equation
$Ag(s)$	0		$Ag(SO_3)_2^{---}$	−226,545	35
$AgCl(s)$	−26,220	Ref. 18	$Ag(NH_3)_2^+$	− 4,003	34
$AgBr(s)$	−22,910	Ref. 15	$HAg(CN)_2$	72,047	29
AgI(hexag.)	−16,356	Ref. 18	$AgCN(s)$	38,499	26
AgI(ppt.)	−15,825	Ref. 15	$Ag(CN)_2^-$	72,047	25

BERKELEY, CALIFORNIA

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

THE DISTRIBUTION OF AMMONIA BETWEEN TOLUENE AND AQUEOUS SILVER AMMONIA CHLORIDE AND HYDROXIDE, AND OF HYDROGEN CYANIDE BETWEEN BENZENE AND AQUEOUS HYDROGEN SILVER CYANIDE[1]

BY MERLE RANDALL AND J. O. HALFORD

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Incidental to the experiments described in the previous paper,[2] we present the following values of the distribution ratio of ammonia between toluene and aqueous silver ammonia chloride and hydroxide at 25°. Column 1 gives the nature of the silver salt, Col. 2 its molality (mole per 1000 g. of water in vacuum), Col. 3 the molality of the total ammonia, Col. 4 the molality of the free NH_4OH based upon the formula $Ag(NH_3)_2^+$ for the complex ion (calculated molality of NH^+ deducted), and Col. 5 the mole fraction of NH_3 in the toluene layer.

TABLE I

DISTRIBUTION OF AMMONIA BETWEEN TOLUENE AND AQUEOUS SILVER AMMONIA CHLORIDE AND HYDROXIDE AT 25°

Silver salt	m $Ag(NH_3)_2$	m Σ base	$m(NH_4OH)$ free	N(NH_3) in toluene	K_{mD}	log K_{mD}
None	.....	0.7347	0.7311	0.0004006	1825	3.261
None	.....	0.8394	0.8355	.0004629	1805	3.257
$Ag(NH_3)_2Cl$	0.0895	1.3039	1.1189	,0006085	1839	3.265
$Ag(NH_3)_2Cl$	.1628	2.1339	1.8007	.0009867	1825	3.261
$Ag(NH_3)_2Cl$	.2151	2.6400	2.2006	.0012054	1826	3.261
$Ag(NH_3)_2OH$	,07352	0.3155	0.09490	.0000520	1825	3 261
$Ag(NH_3)_2OH$	.07535	.3200	.09495	.0000592	1604	3.205
$Ag(NH_3)_2OH$	.07787	.3540	.1231	.0000787	1564	3.194
$Ag(NH_3)_2OH$	.05642[a]	.3392	.1699	.0000952	1784	3.251
$Ag(NH_3)_2OH$	.1525	.6519	.1945	.0001045	1861	3.270
$Ag(NH_3)_2OH$	.1582	.6767	.2021	.0001183	1708	3.232
$Ag(NH_3)_2OH$	.1623	.6950	.2082	.0001120	1859	3.269
$Ag(NH_3)_2OH$	.2033	.8673	.2574	.0001412	1822	3.261
$Ag(NH_3)_2OH$	.2225	.9518	.2841	.0001606	1769	3.248
$Ag(NH_3)_2OH$	.09731[a]	.5831	.2911	.0001660	1754	3.244
$Ag(NH_3)_2OH$	.2888	1.2304	.3642	.0001742	2091	3.320
$Ag(NH_3)_2OH$	.1363[a]	0.7921	.3833	.0002197	1744	3.242
$Ag(NH_3)_2OH$	.1783[a]	0.9691	.4341	.0002539	1710	3.233

[a] Not saturated with $Ag_2O(s)$.

If we assume the activity of the solvent as unity,[3] the constant of the reaction

$$NH_3(g) + H20\ (\text{in } NH_4OH\ (aq.)) = NH_4OH\ \textbf{(aq.)} \qquad (1)$$

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[1] Abridged paper; original received December 22, 1927.

[2] Randall and Halford, THIS JOURNAL, 52, 178 (1930).

[3] See Lewis and Randall, "Thermodynamics and the Free Energy of **Chemical** Substances," McGraw-Hill Book Co., New York, 1923, p. 558.

is independent of the concentration of the ammonium hydroxide up to molal. At the small mole fractions of ammonia in the toluene layer, no great error can be made if we assume the activity of the NH_3 (in toluene) equal to its mole fraction. We therefore write

$$NH_3 \text{ (in toluene)} + H_2O \text{ (in } NH_4OH \text{ (aq.))} = NH_4OH\text{(aq.)}; \; K_D = \gamma' m(NH_4OH\text{(aq.)})/N(NH_3 \text{ in toluene}) = \gamma' K_{mD} \quad (2)$$

where K_D, K_{mD} and γ' are the equilibrium constant, the ratio m/N and the combined activity coefficient of the aqueous ammonia and the water.

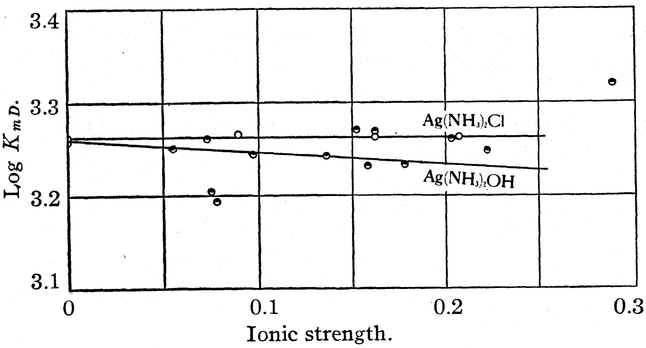

Fig. 1.—Distribution of ammonia between toluene and aqueous silver ammonia chloride or hydroxide.

The values of K_{mD} and of $\log K_{mD}$ are given in Cols. 6 and 7 of Table I. The values of $\log K_{mD}$ are plotted in Fig. 1 against the ionic strength, μ, which is taken as the molality of the silver salt. The values with silver ammonia hydroxide are less concordant than the others because of difficulty of determining the small amount of ammonia in the toluene layer.

From Equation 2

$$\log \gamma' = \log K_D - \log K_{mD} \quad (3)$$

Since the curves of Fig. 1 are approximately straight lines, the logarithm of the activity coefficient of the ammonia is approximately proportional[4] to the ionic strength.

In the case of ammonia in the presence of silver ammonia chloride, we may take $\log \gamma'$ equal to zero. In the case of the silver ammonia hydroxide, the value of $(\log \gamma')/\mu = \mathbf{0.136}$ is about that which would be predicted from that of the chloride and of other substances as given by Randall and Failey.[4]

The assumption that $\log \gamma'$ is a measure of the combined effect of salting out of the ammonia and the lowering of the activity of the water implies that ammonia in the toluene layer is not hydrated. Complete hydration in the toluene layer would eliminate the activity coefficient of the water from the constant of Equation 1. By combining the data of Hantzsch and

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[4] See Randall and Failey, *Chem. Reviews*, 4, 271, 285, 291 (1927).

Vogt[5] on the distribution of ammonia between air and toluene with data on the vapor pressure of aqueous ammonia, the distribution ratio K_{mD} has been calculated for the case in which hydration is impossible. The distribution ratio obtained in this manner is in agreement with our own as given in Table I, and justifies the assumption that the activity coefficient of the water is included in γ'.

If in calculating the distribution coefficient, we employ the mole fraction of ammonium hydroxide in the aqueous phase instead of the molality, we find a positive salting out effect. The calculation of an activity coefficient based on these quantities would not be significant since the activity coefficient is defined as the ratio of the activity to the molality rather than to the mole fraction. Since the activity of the ammonium hydroxide is determined by the mole fraction of ammonia in the toluene layer, it is, of course, independent of the units of concentration employed in the aqueous phase.

The values for the distribution of hydrogen cyanide between benzene and aqueous hydrogen silver cyanide are given in Table II. There is no trend in the values of the distribution coefficient and we may assume that at these low concentrations of the complex acid the activity coefficient of the aqueous hydrogen cyanide may be taken as unity.

TABLE II

DISTRIBUTION OF HYDROGEN CYANIDE BETWEEN BENZENE AND AQUEOUS HYDROGEN SILVER CYANIDE AT 25°

m HCN(aq.)	m $HAg(CN)_2$	N(HCN) in benzene	K_{mD}	m HCN(aq.)	m $HAg(CN)_2$	N(HCN) in benzene	K_{mD}
0.1016	0.00204	0.00228	44.6	0.3625	0.00331	0.00830	43.7
.1234	.00216	.00283	43.6	.1780	.00367	.00401	44.4
.1596	.00245	.00365	43.6	.4230	.00400	.00922	45.9
.2124	.00292	.00492	43.3	.2775	.00425	.00617	44.8
.1825	.00296	.00412	44.3	.4465	.00427	.01065	41.9
.2325	.00316	.00545	42.7	.4830	.00462	.01158	41.6

Summary

The activity coefficient of ammonia in aqueous silver ammonia chloride and of hydrogen cyanide in aqueous hydrogen silver cyanide is unity at 25°. The quotient (log γ')/μ for ammonia in aqueous silver ammonia hydroxide is 0.136 at 25°.

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[5] Hantzsch and Vogt, *Z. physik. Chem.*, 38,701 (1901).

[CONTRIBUTION FROM THE AMERICAN CYANAMID COMPANY]

THE HYDROLYSIS AND POLYMERIZATION OF CYANAMIDE IN ALKALINE SOLUTIONS

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When calcium cyanamide is added to water, hydrolysis of the normal cyanamide occurs, with production of a solution of calcium acid cyanamide and precipitation of calcium hydroxide.[1]

$$2CaCN_2 + 2H_2O \rightleftharpoons Ca(HCN_2)_2 + Ca(OH)_2 \qquad (1)$$

Following the formation of calcium acid cyanamide, a number of reactions may occur, of which the two most important are hydrolysis of the acid cyanamide with production of urea, as represented by

$$Ca(HCN_2)_2 + 4H_2O \rightleftharpoons 2NH_2CONH_2 + Ca(OH)_2 \qquad (2)$$

and polymerization to produce dicyandiamide, as represented by

$$Ca(HCN_2)_2 + 2H_2O \rightleftharpoons NH_2C{=}NHNHCN + Ca(OH)_2 \qquad (3)$$

Secondary reactions also may occur, dicyandiamide being hydrolyzed to guanylurea or to cyanurea, and urea to ammonium carbonate.

It has long been known that the reactions of cyanamide in alkaline solutions are dependent upon the nature of the base present. The facts have been summarized as follows:[2] "The strong alkalies KOH or NaOH in aqueous solutions produce almost entirely urea with no trace of dicyandiamide; weak alkalies, NH_4OH or MgO, produce dicyandiamide almost exclusively at first, and then ammonia. CaO, however, produces a mixture of urea, dicyandiamide, ammeline, amidodicyanic acid, ammonia and other bodies."

It must be carefully emphasized that the reactions occurring in soil solutions are not necessarily the same as those in ordinary aqueous solutions. In the former such variables as colloids, bacteria and the like have important effects upon the course of the reactions. It remains true, however, that one cannot expect fully to understand the reactions of cyanamide in a system as complex as is the soil unless he first understands its reactions in water alone.

That cyanamide is readily converted to other products was noted long before the development of the modern Cyanamid industry. Cloëz and Cannizzaro[3] observed that a compound of the same empirical formula but with markedly different properties was spontaneously formed when

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[1] Drechsel, *J. prakt. Chem.*, [2] 16, 210 (1887); Kappen, *Landw. Vers. Sta.*, **68**, 301 (1908); Ulpiani, *Gazz. chim. ital.*, II, **38**, 358 (1908); I, 40, 613 (1910).

[2] Pranke, "Cyanamid," Chemical Publishing Co., 1913.

[3] Cloez and Cannizzaro, *Ann.*, 78, 228 (1851).

solutions of cyanamide were allowed to evaporate. They named this new product cyanuramin—it was undoubtedly dicyandiamide. The same observers reported that alkalies decomposed cyanamide, although they did not mention the products formed. Other early observers were aware of the formation of polymerized products, variously styled, and of urea.[4]

The first attempt at a quantitative study of the reactions of calcium cyanamide in alkaline solutions was made by Grube and his co-workers.[5] They found that the concentration of the alkali had a marked effect upon the velocity of decomposition of cyanamide, the velocity increasing and then decreasing with increasing alkali concentration. As a result of their work a process for the manufacture of dicyandiamide was worked out, styled by the inventors the "Process of Optimum Lime Concentration."[6] According to their procedure a solution of calcium acid cyanamide was first prepared, and to this solution sulfuric acid was added in varying amounts and at varying time intervals. The additions were to be made in accordance with the theory that there should always be present in the solution four moles of cyanamide for each mole of lime, this ratio being considered the "optimum" for dicyandiamide formation. The mechanism of the reaction, according to these workers, is that dicyandiamide is formed by reaction between an undissociated cyanamide molecule and *a* cyanamide ion, as represented by the equation

$$(\mathrm{NHCN})^- + \mathrm{H_2NCN} = (\mathrm{NHC{=\!=}NHNHCN})^-$$

Morrel and Burgen[7] also studied the kinetics of the formation of dicyandiamide from cyanamide and arrived at the same conclusion, namely, that the reaction is ionic. This theory, announced almost simultaneously by Grube and Krüger and by Morrell and Burgen, is discussed more fully in a later section of the present paper where we have shown that our own data are consistent with and confirmatory to the ionic theory.

Hetherington and Braham[8] studied the polymerization and hydrolysis of cyanamide in aqueous alkaline solutions. Earlier investigators had assumed that the cyanamide disappearing was completely transformed to dicyandiamide, an assumption which our data show to be true only under special conditions. Hetherington and Braham determined cyanamide disappearing and urea formed. Dicyandiamide formed was arrived at by difference. A summary of their results is shown below.

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[4] Ulpiani, *Gazz. chim. ital.*, II, **38**, 358 (1908); I, **40**, 613 (1910); Haag, *Ann.*, **122**, 23 (1862); Baumann, *Ber.*, **6**, 1371 (1873); Beilstein and Geuther, *Ann.*, **108**, 99 (1858); **123**, 241 (1862).

[5] Grube and Kruger, *Z. physik. Chem.*, **86**, 65 (1913); Grube and Nitsche, *Z. angew. Chem.*, *I*, *27*, 368 (1914).

[6] Grube and Nitsche, German Patent 279,133, June 5, 1913.

[7] Morrell and Burgen, *J. Chem. Soc.*, **105**, 576 (1914).

[8] Hetherington and Braham, THIS JOURNAL, **45**, 828 (1923).

Cyanamide at start 0.5 M. Temperature 50°

NaOH, moles/l.	After 1 hour, % of total nitrogen present as			After 2 hours, % of total nitrogen present as		
	Cyan. N	Urea N	Dicyan.[a] N	Cyan. N	Urea N	Dicyan.[a] N
0.01	92.1	2.9	5.0	90.4	3.3	6.3
0.1	69.6	3.2	27.2	55.6	3.8	40.6
1.0	94.0	5.0	1.0	92.3	7.0	0.7

NaOH, mole/l.	After 3 hours, % of total nitrogen present as			After 20 hours % of total nitrogen present as		
	Cyan. N	Urea N	Dicyan.[a] N	Cyan. N	Urea N	Dicyan.[a] N
0.01	85.8	3.3	10.9	47.2	4.9	47.9
0.1	44.4	4.1	51.5	14.1	10.1	75.8
1.0	89.3	8.3	2.4	62.7	34.4	2.9

[a] Dicyandiamide obtained by difference.

Hetherington and Braham's results show that in alkaline solution urea is formed as well as dicyandiamide, increased concentrations of alkali resulting in increased urea formation. Hetherington and Braham concluded that their results with respect to dicyandiamide formation could be explained by the theory of Grube and Krüger. The formation of urea was attributed to the catalytic effect of hydroxyl ions.

Although it seems readily apparent that effects such as those reported by the previous investigators are controlled by hydrogen-ion concentration, the problem had not heretofore been studied from this point of view. It therefore became the purpose of the work which is here reported to study the influence of hydrogen-ion concentration upon the fate of cyanamide in alkaline solutions. In the experiments, the details of which are recorded below, the course of cyanamide disappearance and urea and dicyandiamide formation was observed in solutions whose hydrogen-ion concentration was maintained at constant values.

Dicyandiamide Formation

Experimental Method

Cyanamide Solutions.—Commercial calcium cyanamide was agitated for one hour with three times its weight of water at 30° and filtered. To the filtrate dilute sulfuric acid was added carefully and with vigorous stirring, the temperature being maintained below 30°. The sulfuric acid addition was continued until the solution was just acid to methyl red indicator (about PH 5), and the precipitated calcium sulfate was filtered off. Solutions of cyanamide prepared in this way and kept at ordinary room temperature suffer practically no change in cyanamide concentration over a period of several months.

Buffer Solutions.—For the measurements at PH 6 sodium dihydrogen phosphate and sodium hydroxide were employed as the buffer combination. For *P*H 8 to *P*H 10 sodium hydroxide–boric acid solutions were used. The buffer solutions used were all more concentrated than those usually employed (0.5 molal phosphate or borate instead of 0.2 molal). As will appear from the data the buffering was very good throughout this range. For hydrogen-ion concentrations lower than PH 10, sodium hydroxide was used because suitable buffer combinations were not available. Alkalinity control was consequently poor.

Methods of Analysis.—Cyanamide was determined by precipitating it as silver cyanamide from an ammoniacal solution, filtering, washing and determining nitrogen in the precipitate by the Kjeldahl method.

Urea was determined by the urease method.

Dicyandiamide was determined by hydrolyzing to guanylurea under carefully controlled conditions, precipitating guanylurea picrate by the addition of picric acid and weighing. Details of the method are as follows. A 10-cc. sample is pipetted into a 150-cc. beaker and 25 cc. of hydrochloric acid solution (one volume of sp. gr. 1.18 mixed with two volumes of water) added. The beaker is suspended over a gently boiling water-bath so that the bottom of the beaker almost touches the water and is held there for fifteen minutes. The solution is then cooled, made slightly alkaline to phenolphthalein with 10% sodium hydroxide solution, and made up to 100 cc. in a volumetric flask. To a 25-cc. aliquot of this solution, 5 cc. of an alcoholic solution of picric acid (6 g. of picric acid in 100 cc. of 95% ethyl alcohol) is added. The solution is allowed to stand for one hour with occasional stirring and is then filtered through a tared Gooch crucible. A saturated solution of guanylurea picrate is used for washing. The precipitate is dried at 105° for one hour. A solubility correction of 0.0044 g. is added to the weight of the precipitate. The factor for conversion of the weight of guanylurea picrate to dicyandiamide nitrogen is 0.169. The quantity of picric acid recommended is sufficient for about 0.2 g. of guanylurea picrate.

Melamine, guanylurea and guanidine were tested for by means of picric acid with negative results in all of the experiments.

Measurement of the Hydrogen-Ion Concentration.—Hydrogen-ion concentrations were determined by potentiometer measurements with a hydrogen electrode immersed in the solution. A saturated potassium chloride calomel cell was used as the other electrode. The chain was at 50°. The value of the chain

$$\text{Hg–HgCl} - \text{satd. KCl} - \text{satd. KCl} - 0.1\ M\ \text{HCl} - \text{H}_2\text{(Pt)}$$

was checked at intervals and found to agree with the value reported by Fales and Mudge for 50°.[9] The hydrogen-ion concentration was calculated from the e.m.f. measurement by means of the Nernst equation, which for this temperature and chain is

$$P_{\text{H}^+} = 15.60E - 3.61$$

Procedure.—In a water-bath at 50 ± 0.1° were placed bottles containing the necessary buffer solutions, a wash bottle containing distilled water and, in a standard 200-cc. flask, exactly enough cyanamide solution to contain 2.80 g. of cyanamide nitrogen. When all had reached the temperature of the bath, the proper amounts of buffer solutions were pipetted into the cyanamide solutions, distilled water was added to make the volume up to 200 cc. (0.5 molal) and the contents of the flasks were mixed as quickly as possible. The initial time was taken at the moment when the additions of buffer solutions had been completed. Samples were withdrawn immediately for analysis and subsequently at various time intervals as indicated in the tables. Immediately after samples were withdrawn, they were made neutral to methyl red to prevent further reaction.

In the tables the velocity constants, k_{D}, for the polymerization of cyanamide to dicyandiamide are calculated by means of the formula for a reaction of the second order

$$k_{\text{D}} = \frac{1}{t}\frac{x}{c(c-x)}$$

where c is the initial concentration of cyanamide, in grams of nitrogen

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[9] Fales and Mudge, This Journal, 42,2434 (1920).

per 100 cc., and x is the change in concentration occurring in the time interval, t, in hours.

For the hydrolysis to urea and for the decomposition of dicyandiamide the velocity constants k_U and k_D1 are calculated for a reaction of the first order

$$k = \frac{1}{t} \log \frac{c}{c - x}$$

Table I summarizes the results of this study over the range PH 6 to **PH 12.** The relation between the velocity constants and the hydrogen-ion concentrations is shown graphically in Fig. 1.

TABLE I

RESULTS OR EXPERIMENTS

Time, hours	PH	Found, g. of nitrogen per 100 cc. Cyanamide	Dicyandiamide	Urea	Sum	Formed, g. of nitrogen per 100 cc. Dicyandiamide	Urea	Velocity constant. k_D
0.0	6.0	1.25	0.30	0.02	1.57	0.00	0.00	
.5	..	1.23	.32	..		.02	..	
1.5	..	1.31	.34	..		.04	..	
5.5	..	1.23	.32	..		..	..	
143.5	..	1.16	.35	.03	1.54	.05	..	
0.0	8.4	1.31	.23	.12	1.66	.00	.00	....
1.0	..	1.21	.31	..		.08	..	....
2.0	..	1.07	.47	..		.24	..	8.6 X 10^{-2}
4.0	..	0.96	.60	..		.37	..	7.2 X 10^{-2}
6.0	8.4	.85	.72	.		.49	..	7.3 × 10^{-2}
24.0	..	..	..	.16		..	.04	....
72.0	..	.00	1.31	..		1.08	..	....
						Average for PH 8.4,		7.7 × 10^{-2}
0.0	8.9	1.31	0.23	.12	1.66	0.00	.00	....
1.0	..	0.96	.49	..		.26	..	21 × 10^{-2}
2.0	..	.75	.70	..		.47	..	24 X 10^{-2}
4.0	..	.65	.95	..		.72	..	21 X 10^{-2}
6.0	9.1	.53	1.09	..		.86	..	21 X 10^{-2}
24.0	..	.13	1.35	.18	1.66	1.12	.06	....
72.0	..	.00	1.39	..		1.16	..	....
						Average for PH 9.0,		22 × 10^{-2}
0.0	9.3	1.32	0.19	.07	1.58	0.00	.00	....
1.0	9.4	0.94	.58	..		.39	..	31 X 10^{-2}
2.0	9.5	.69	.77	..		.58	..	32 X 10^{-2}
4.0	9.6	.47	1.03	..		.84	..	34 X 10^{-2}
6.0	9.6	.34	1.14	..		.95	..	37 X 10^{-2}
24.0	9.8	.12	1.36	..		1.17	..	31 × 10^{-2}
72.0	9.9	.05	1.36	.10	1.51	1.17	.03	....
						Average for PH 9.6,		33 × 10^{-2}
0.0	10.3	1.39	0.20	.07	1.66	0.00	.00	....
1.0	..	1.02	.50	..		.30	..	21 X 10^{-2}
2.0	10.7	0.83	.68	..		.48	..	21 X 10^{-2}
4.0	..	.69	.83	..		.63	..	16 X 10^{-2}

TABLE I (*Concluded*)

Time, hours	P_H	Found, g. of nitrogen per 100 cc. Cyanamide	Dicyandiamide	Urea	Sum	Formed, g of nitrogen per 100 cc. Dicyandiamide	Urea	Velocity constant, k_D
6.0	..	0.62	0.93	..		0.73	..	14×10^{-2}
24.0	..	.30	1.05	.12	1.47	.85	.05	....
48.0	11.3	..	1.07	..		.87	..	....
						Average for P_H 10.5,		21×10^{-2}
0.0	11.4	1.39	0.20	.07	1.66	0.00	.00	....
1.0	..	1.32	.26	..		.06	..	....
2.0	..	1.28	.28	..		.08	..	3.1×10^{-2}
4.0	..	1.19	.32	..		.12	..	3.0×10^{-2}
6.0	..	1.06	.35	..		.15	..	2.3×10^{-2}
24.0	12.1	0.72	.37	.15		.17	.08	2.8×10^{-2}
48.0	..	.49	.26	.23	0.98	.06	.16	2.8×10^{-2}
						Average for P_H 11.4,		3.1×10^{-2}

The data of Table I may be summarized as follows: (1) At constant hydrogen-ion concentration the polymerization of cyanamide to dicyandiamide proceeds as a reaction of the second order. *(2)* The velocity of the reaction is a function of the hydrogen-ion concentration. **(3)** The velocity of formation of dicyandiamide is at a maximum at P_H 9.6 and decreases rapidly at hydrogen-ion concentrations above or below this point. (4) Urea formation is negligible throughout this range of hydrogen-ion concentration. (5) Cyanamide disappearing is quantitatively accounted for by dicyandiamide produced up to about P_H 10. Above P_H 10, nitrogen accounted for as dicyandiamide and urea is significantly less than the cyanamide disappearing. That this is due to dicyandiamide destruction is shown in a later section of this paper.

It is of interest to attempt a correlation of the velocity constants of dicyandiamide formation shown in our table with the theory of Grube and Krüger,[5] which, it will be recalled, states that dicyandiamide is formed by reaction between a cyanamide molecule and a cyanamide ion.

$$(\mathrm{NHCN})^- + \mathrm{H_2CN_2} \rightleftarrows (\mathrm{NHCNHNHCN})^-$$

According to this theory

$$\frac{dx}{dt} = g(\mathrm{H\ Cy})(\mathrm{Cy}^-) \qquad (1)$$

where g is the velocity constant of the reaction.

The ionization constant, K, of cyanamide is given by

$$\frac{\mathrm{H}^+ \times \mathrm{Cy}^-}{\mathrm{H\ Cy}} = K \quad \text{or} \qquad (2)$$

$$\frac{\mathrm{Cy}^-}{\mathrm{H\ Cy}} = \frac{\mathrm{K}}{\mathrm{H}^+} \qquad (3)$$

Adding one (1) to both sides of this equation, we have

$$\frac{\mathrm{Cy}^- + \mathrm{H\ Cy}}{\mathrm{H\ Cy}} = \frac{\mathrm{K} + \mathrm{H}^+}{\mathrm{H}^+} \qquad (4)$$

Since

$$Cy^- + H\,Cy = (c - x) \tag{5}$$

$$H\,Cy = (c - x)\frac{H^+}{K + H^+} \tag{6}$$

In a similar manner it can be shown that

$$Cy^- = (c - x)\frac{K}{K + H^+} \tag{7}$$

On substitution of values given by (6) and (7), Equation 1 becomes

$$\frac{dx}{dt} = (c - x)^2 g \frac{K\,H^+}{(K + H^+)^2} \tag{8}$$

Our experimental work has shown that

$$\frac{dx}{dt} = k_D(c - x)^2 \tag{9}$$

where k_D is a function of H^+

Therefore

$$k_D = g\frac{K\,H^+}{(K + H^+)^2} \tag{10}$$

The ionization constant, K, of cyanamide is given by Kamayama[10] as 20.1×10^{-11} at 50°. Thus

$$K = 20.1 \times 10^{-11} = 10^{-9.7} \tag{11}$$

Using this value of K in (10) we have the equation giving k_D as a function of H

$$k_D = g\frac{10^{-9.7}\,H^+}{(10^{-9.7} + H^+)^2} \tag{12}$$

From Equation 12 it may be seen that, knowing the value of k_D for any value of H^+, we may calculate the constant g. Then knowing **g,** we may calculate k_D for any value of H^+. In other words, if we know the velocity constant at any one hydrogen-ion concentration, it is possible to calculate it for any other hydrogen-ion concentration. In the following table we have taken the value of k_D for PH 8.4, and from it have calculated the velocity constants for the hydrogen-ion concentrations at which our experiments were conducted.

TABLE II

OBSERVED AND CALCULATED CONSTANTS

P_H^+	8.4	9.0	9.6	10.5	11.4
k_D observed	7.7×10^{-2}	21×10^{-2}	33×10^{-2}	21×10^{-2}	3.1×10^{-2}
k_D calculated	....	21×10^{-2}	38×10^{-2}	21×10^{-2}	3.1×10^{-2}

Formation of Urea in Highly Alkaline Solutions.—We have seen from the data already presented that dicyandiamide is practically the only product obtained from solutions of cyanamide up to about PH 10. Above PH 10 the rate of dicyandiamide formation became slower and at the highest PH studied, PH 12, small amounts of urea were being formed. This

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[10] Kamayama, *Trans. Am. Electrochem. Soc.*, *40*, 131 (1921).

suggested a few experiments on the fate of cyanamide in highly alkaline solutions. The data of this work are shown in Table III.

TABLE III

RESULTS OF EXPERIMENTS

Time, hrs.	Normality of NaOH	PH	N₂ per 100 cc., g. Cyanamide	Dicyandiamide	Urea	Velocity constant, k_U
0	0.49	12.6	1.40	0.00	0.00	....
21	..		0.88	.00	.41	0.96×10^{-2}
41			.57	.00	.63	$.95 \times 10^{-2}$
89			.28	.00	.98	$.79 \times 10^{-2}$
113	..		.20	.00	1.11	$.74 \times 10^{-2}$
168	..	13.4	.10	.00	1.26	....
0	0.68	12.9	1.40	.00	0.00	....
21	..		0.93	.00	.44	$.85 \times 10^{-2}$
69	..		.42	.00	.88	$.76 \times 10^{-2}$
93			.28	.00	1.04	$.83 \times 10^{-2}$
168	..	13.5	.10	.00	1.24	....
0	1.00	13.4	1.40	.00	0.00	....
21	..		..	.00	.38	....
69	..		0.42	.00	.86	$.76 \times 10^{-2}$
93	..		.28	.00	1.05	$.83 \times 10^{-2}$
168	..	13.6	.11	.00	1.23	....

The conclusions which may be derived from these data are as follows. (1) Cyanamide disappearing is quantitatively accounted for by urea formed. (2) The hydrolysis of cyanamide to urea in alkaline solutions is a reaction of the first order. (3) In the range studied the reaction velocity is independent of the alkali concentration.

We conclude from the data of Tables III and I that the hydrolysis of cyanamide in alkaline solutions is a reaction of cyanamide ion, and that the velocity of the hydrolysis is proportional to the concentration of this ion. When sufficient alkali is present to convert all the cyanamide into the salt, further addition of alkali has no further effect on the rate of hydrolysis.

Dicyandiamide Destruction.—The data of Table I show that at the higher alkalinities the cyanamide disappearing cannot be accounted for by urea and dicyandiamide produced. That this is in part at least due to destruction of dicyandiamide is indicated by the dicyandiamide analyses of the solution maintained at PH 11, where it was found that the dicyandiamide content of the solution was reduced by one-half between the twenty-fourth and the forty-eighth hours.

This led to an investigation of the stability of dicyandiamide at various hydrogen-ion concentrations. The methods were the same as those employed in the previous work. Pure dicyandiamide was dissolved in the buffered solutions and its concentration determined after various intervals of time. The data are shown in Table IV and graphically in Fig. 1.

TABLE IV

EXPERIMENTAL DATA

Time, hours	P_{H^+}	N₂ per 100 cc., g. Dicyandiamide found	Dicyandiamide destroyed	Velocity constant, k_{DI}
0.0	9.3	1.057	...	
24.0		1.035	...	
72.0		1.057	0.000	
168.0		1.058	.000	0
0.0	9.8	1.009	...	
24.0		1.000	.009	
72.0		0.998	.011	
168.0		.985	.024	6.9×10^{-5}
0.0	10.3	1.020	...	
24.0		1.018	.002	
		...	...	
168.0		0.950	.070	1.23×10^{-4}
0.0	11.0	.939		
24.0		.901	.028	
72.0		.890	.049	
168.0		.827	.112	3.23×10^{-4}
0.0	11.4	1.047	...	
24.0		0.940	.107	
72.0		.835	.212	1.36×10^{-3}

It will be seen that dicyandiamide is relatively stable up to PH 10. Above *P*H 10 dicyandiamide is destroyed, the rate increasing with increasing *P*H. The nature of the products thus formed was not studied; cyanurea is known to be formed under these conditions.[11]

Effect of Temperature on Hydrogen-Ion Concentration **Optimum** for Polymerization.—On page 196 we considered the Optimum Lime Process of Grube, which was based upon the maintenance of equal concentrations of cyanamide ions and undissociated cyanamide. That this condition necessitates maintenance of the hydrogen-ion concentration at a constant value is proved as follows. In any solution containing cyanamide

$$\frac{H^+ (Cy)^-}{H\ Cy} = K$$

$$\text{If } (Cy)^- = H\ Cy \text{ then } H^+ = K$$

This relation may also be derived from Equation 10.

The value of K at 50°, as was noted above, was found by Kamayama to be $10^{-9.7}$, which our work has shown to be the optimum hydrogen-ion concentration for the polymerization of cyanamide to dicyandiamide. This relationship between H^+ and K holds regardless of the temperature. Since Kamayama has reported the ionization constants for cyanamide at various temperatures, we may adopt his values as the optimum hydro-

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[11] Hallwachs, *Ann.*, 153, 295 (1870); Ulpiani, *Gazz. chim. ital.*, II, **38**, **358** (1908); I, 40, 613 (1910).

gen-ion concentration for the temperatures in question. His values are given in Table V.

TABLE V

VALUES OF KAMAYAMA

Temp., °C.	0	25	50	80	100
K × 10^{11}	1.15	5.42	20.1	75.6	163
*P*H	10.4	10.3	9.7	9.1	8.8

Reactions of Cyanamide in **the** Soil.—In view of the fact that the *P*H of soil solutions in humid regions is usually less than 7, it will be evident

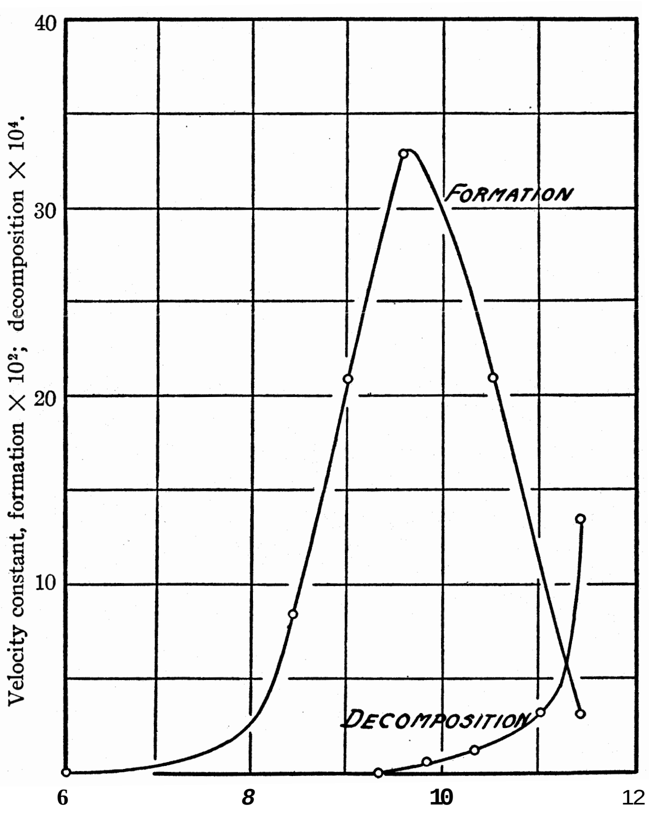

Fig. 1.—Effect of *P*H on velocities of formation and decomposition of dicyandiamide.

from the data which we have presented that dicyandiamide cannot normally be formed when calcium cyanamide is applied to the soil. Even at 50° our results show negligible dicyandiamide formation at this PH, while at lower temperatures not only is the reaction velocity greatly reduced but the limiting PH for dicyandiamide formation is raised.

The occasional finding of dicyandiamide reported by some investigators is clearly attributable to improper conditions of application. Calcium cyanamide is an alkaline material and should be applied is such a manner that its alkalinity does not exceed the buffering capacity of the soil. This necessitates proper distribution so that local high concentrations of alkalinity are avoided and suggests special care when calcium cyanamide is applied to sandy soils deficient in humus and other colloidal materials.

Many studies of the fate of calcium cyanamide in the soil are reported in the literature and the conclusion reached that cyanamide is converted to urea.[12] In our experiments urea formation was negligible in solutions of low PH. This difference between ordinary aqueous solutions and soil solutions is to be ascribed to the catalytic effect of the soil colloids. That the conversion of cyanamide to urea is catalyzed by such substances has been shown by many investigators. Kappen in particular in his elaborate "Dissertation" (Die Katalyse des Cyanamids und ihre Bedeutung für die Landwirtschaft) has called attention to the catalytic action of soil colloids, metallic oxides and hydroxides, and has, in fact, obtained a long series of patents on the production of urea from calcium cyanamide by agitating it with water in the presence of such catalytic materials.[13]

Addendum.—Subsequent to the preparation of the above paper, our attention was called to an article by Cochet on the polymerization of cyanamide to dicyandiamide as a function of hydrogen-ion concentration.[14] Cochet did not buffer his solutions and very marked changes in hydrogen-ion concentration occurred during the course of the experiments, a fact to which attention is called by the author. His results are in entire accord with our own, when the increasing PH observed in his experiments is taken into account. Cochet concludes that the polymerization reaction reaches an equilibrium at the end of 165 hours. We are of the opinion that the equilibrium is only an apparent one and that the reaction velocity has been reduced by the rise in the *P*H.

Cochet reports that cyanamide in the soil is rapidly transformed into urea.

The authors wish to express their thanks to Mr. P. W. Griffith for valuable assistance.

Summary

1. The influence of hydrogen-ion concentration on the reactions of cyanamide in aqueous solution has been studied from PH 6 to PH 13 at 50°.

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[12] Ulpiani, *Gazz. chim. ital.*, II, 38, 358 (1908); 1, 40, 613 (1910); Seelhorst, *J. Landw.*, 53, 323 (1905); Stutzer and Reis, *ibid.*, 58, 65 (1910); Kappen, "Die Katalyse des Cyanamids und ihre Bedeutung fur die Landwirtschaft," Dissertation, Jena, 1913.

[13] Immendorf and Kappen, U. S. Patent 1,048,699; British Patents 17,018, 20,611; German Patents 254,474; 256,524, 256,525; 257,642; 257,643 and 267,206.

[14] Cochet, Congrès des Engrais Azotés de Synthèse, May, 1927, p. 34.

2. Polymerization to dicyandiamide takes place quantitatively in alkaline solution up to PH 10.

3. The velocity of dicyandiamide formation is a function of the hydrogen-ion concentration. It reaches a maximum at PH 9.6 and decreases rapidly below or above this PH.

4. Above PH 12 cyanamide is hydrolyzed quantitatively to urea.

5. The rate of hydrolysis is independent of alkalinity in the range studied.

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

THE POLARITIES AND THE ORIENTING INFLUENCES OF SUBSTITUTES IN THE BENZENE RING

BY WENDELL M. LATIMER AND C. W. PORTER

RECEIVED JUNE 5, 1929 PUBLISHED JANUARY 8, 1930

More than fifty years ago it was observed that certain groups, when substituted for hydrogen in benzene, direct the next entering group to the meta position and that other groups direct to the ortho and para positions. There have been many attempts to classify atoms and groups on the basis of this behavior.[1] The most successful theory (proposed by Lapworth[2] and Stieglitz[3] and supported and amplified by many others) assumes alternate polarities in the carbon atoms of the benzene ring, induced by the electronegative or electropositive character of the first substituted group. The theory is based upon arbitrary qualitative estimates of polarity.

We wish to present in this paper a system which gives at least a semi-quantitative basis for determining polarity and which may, therefore, serve as a means of classifying groups exerting different orienting influences.

Our plan is to estimate, from considerations of electronic configurations, the residual charge on the atom attached to the ring. When a pair of electrons is shared between two atoms, we assume, except in the case of hydrogen, that the electrons are quantized in respect to the field between the atoms and that the effect of their charges is distributed between the atoms in the ratio of the positive charges on the two kernels. Thus we consider a pair of electrons between carbon and nitrogen as contributing 2 X 4/9 electron charges to the carbon atom and 2 X 5/9 electron charges to the nitrogen.

The bond between hydrogen and another atom cannot be so treated, as

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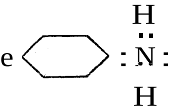
[1] The following are important references to the earlier literature: (a) Hübner, *Ber.*, 8, 873 (1875); (b) Noelting, *ibid.*, 9, 1797 (1876); (c) Armstrong, *J. Chem. Soc.*, **51**, 258 (1887); (d) Crum-Brown and Gibson, *ibid.*, 61, 367 (1892); (e) Flürscheim, *J. prakt. Chem.*, **66**, 32 (1902); (f) Fry, THIS JOURNAL, 38, 1323 (1916).

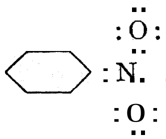
[2] Lapworth, *J. Chem. Soc.*, 121, 1391 (1922).

[3] Stieglitz, THIS JOURNAL, 44, 1299 (1922).

the moments of inertia of hydrides, obtained from band spectra, indicate that the hydrogen ion is within the electron shell or at least very close to the position of maximum electron density. Hence in this case we consider that two electrons and one proton are so close together that their resultant charge is minus one.

On this basis we may calculate, as an example, the resultant charge on the nitrogen of aniline  $C_6H_5:\overset{\cdot\cdot}{\underset{H}{\overset{H}{N}}}:$ The positive charge on the nitrogen kernel is five. This is reduced by two unshared electrons, four electrons shared with hydrogen and two shared with carbon. The residual charge then is

$$+5 - 2 - (4 \times 1/2) - (2 \times 5/9) = -0.11$$

Dealing with nitrobenzene,  $C_6H_5:\underset{:\underset{\cdot\cdot}{O}:}{\overset{:\overset{\cdot\cdot}{O}:}{N}}.$, in the same way, we have for the residual charge

$$+5 - (4 \times 5/11) - (2 \times 5/9) = 4\text{-}2.07$$

Similar calculations for a large number of groups and atoms are summarized in Table I.

TABLE I

RESIDUAL CHARGE AND DIRECTING INFLUENCE OF SUBSTITUENT GROUPS IN BENZENE

Group	Residual charge	Principal orienting influence	Group	Residual charge	Principal orienting influence
$—OR$	-0.4	$p + o$	$—CHX_2$	$+0.55$	$p + o$
$—X$ (halogen)	-0.27	$p + o$	$—CBr_2NO_2$	$+0.65$	m
$—OH$	-0.2	$p + o$	$—CX_3$	$+0.82$	m[a]
$—NH_2$	-0.11	$p + o$	$—\overset{+}{N}H_3$	$+0.88$	m
$—NH_2COR$	-0.11	$p + o$	$—\overset{+}{N}R_3$	$+0.88$	m
$—N=N—C_6H_5$	-0.11	$p + o$	$—NHOH$	$+1.0$	m
$—CH_3$	0	$p + o$	$—CHO$	$+1.20$	m
$—C_nH_{2n+1}$	0	$p + o$	$—COCH_3$	$+1.20$	m
$—C_6H_5$	0	$p + o$	$—C\equiv N$	$+1.2$	m
$—CH_2COOH$	0	$p + o$	$—CONH_2$	$+1.32$	m
$—CR_2NO_2$	$+0.11$	$p + o$	$—CONHR$	$+1.32$	m
$—CHRNH_2$	$+0.11$	$p + o$	$—COCl$	$+1.38$	m
$—C=CH_2$ $\mid$ $O—CH_3$	$+0.2$	$p + o$	$—COOH$	$+1.4$	m
$—N=O$	$+0.2$	$p + o$	$—SO_3H$	$+1.8$	m
$—CH_2X$	$+0.27$	$p + o$	$—NO_2$	$+2.1$	m

[a] p and o in chlorinations and m in nitrations.

It will be observed that if the residual charge on the atom attached to the ring has a high positive value, the substituent directs to the meta position.

If the value is negative or zero, the group directs to the ortho and para positions. As the rule represepts only a first approximation to a true solution of the problem, the line of division is not sharp and in general values between +0.1 and +0.6 lead to mixtures of para, ortho and meta compounds with large percentages of each.

An obvious inaccuracy in the method is the failure to take into account the decrease in the effective positive charge of the kernels by distortion or shielding effects of the orbits of electrons not directly involved in the bond. Thus actually there must be a difference between the residual carbon charges in CF_3, CCl_3, CBr_3 and CI_3: the distortion of the electron shells in the larger ions will tend to decrease the effective positive charge on their kernels making the carbon in CI_3 more negative than in CF_3, though in the case of the lighter elements such effects are probably not large.

In the case of unsaturated compounds it is especially arbitrary to assign positions to the electrons since we do not know how many electrons are in the bonds. In Table I we have used the ordinary symbol for double bond, =, as indicating four electrons shared; in all other cases the bond is considered as a single pair. In the so-called carbon–oxygen double bonds of carboxyl, aldehyde, etc., we have assumed a single electron pair in the belief that the large difference in the electronegative character of oxygen and carbon renders it unlikely that the carbon can pull four electrons into the bond. This is also in agreement with the symmetrical arrangement of the oxygen atoms about carbon in solid carbonates. Por the same reason we assume for the structure of the cyanide ion, $:C::\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}$, rather than a six electron bond. However, the nature of an unsaturated nitrogen—xygen bond is more uncertain, as oxygen is not much more electronegative than nitrogen. In these cases we have assumed a double electron bond in the NO_2 group where there are two oxygen atoms competing with a single nitrogen atom, but a four electron bond in the NO group. Actually these represent limiting conditions and our values for nitro, carboxyl, aldehyde, etc., are probably somewhat too positive and for the nitroso group too negative.

The system used in the calculations does not take into account atoms beyond those directly connected with the key atom, though these may in certain cases have considerable influence. An example of this, discussed by Fliirscheim and Holmes,[4] is COOH which, in benzoic acid, directs meta, and COO– which, in the benzoate ion, directs ortho and para, the latter being an exception to our rule. In the free acid the resultant field acting upon the benzene ring is positive, as determined by the residual charge upon the carbon of the carbonyl group. In the ion the negative field due to the unneutralized charge is superimposed to such an extent that the sign of the

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[4] Flürscheim and Holmes, *J. Chem. Soc.*, **128,1562** (1926).

resultant field is changed. Likewise the positive charges on NH_3^+ and on NR_3^+ probably render them more strongly meta orienting than indicated by our figures.

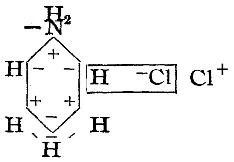
Ingold's[5] observation that the group $CH_3{-}O{-}\overset{|}{C}{=}CH_2$ directs to the ortho and para positions is in harmony with our system of classification. This was regarded as an exceptional case when the oxygen atom was used as the key atom in determining the position of induced positive charges in the ring; and in general the results obtained clearly indicated that the actual orienting influence of a group is determined by its positive or negative character, as given by this semi-quantitative treatment.

Holleman lists certain groups in the order of their meta directing capacities as follows:[6] $COOH > SO_3H > NO_2$. The order was determined with reference to the position taken by a third group in a ring containing two of these radicals. The presence of two groups complicates the problem by destroying the balance which normally exists in the benzene ring (see later discussion of this point). The more direct evidence based upon the percentages of ortho, meta and para derivatives formed from monosubstitution products is given below. The figures indicate the percentage of meta derivative obtained from each by treatment with nitric acid.

	C_6H_5COOH[7]	$C_6H_5SO_3H$[8]	$C_6H_5NO_2$[9]
% meta	82%	90%	93%
Charge (Table I)	+1.4	+1.8	+2.1

These values substantiate our order, although it is not to be expected that this type of evidence will in every case give agreement, especially when derived from very different experimental conditions.

While the effect of polarity upon orientation may be accepted as an experimental observation, the explanation of this behavior obviously depends upon a knowledge of the structure of the benzene ring. The theory proposed by Lapworth and by Stieglitz of induced polarity of opposite signs on alternate carbon atoms appears to make a satisfactory start. Thus the action of chlorine upon aniline was pictured as indicated. The chlorine molecule splits to give a negative chloride ion, which combines with a hydrogen ion. The positive chlorine combines with a negative carbon, in this case para and ortho, to the negative nitrogen. The same mechanism applies to all the other types of direct substitution, i. e., Br, NO_2 or SO_3H, since all of these involve the



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[5] Ingold and Ingold, *J. Chem. Soc.*, 127, 870 (1925).

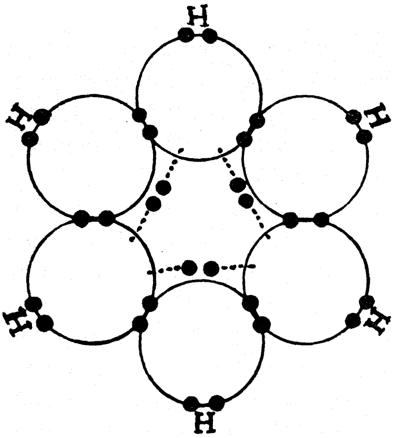
[6] A. F. Holleman, "Die direkte Einfuhrung von Substituenten in den Benzolkern," 1910, p. 469.

[7] "Annual Reports on the Progress of Chemistry," London, 1927, p. 151.

[8] A. F. Holleman, Ref. 6, p. 75.

[9] "Annual Reports on the Progress of Chemistry," London, 1926, p. 132.

splitting of the oxidizing agent into a negative ion which joins with a hydrogen ion and a positive ion which combines with a negative carbon.



One interpretation of this picture in terms of an electronic structure of the benzene ring would be that alternate carbon atoms of the ring possess or share six and eight electrons, respectively. This, doubtless, is a limiting condition, the actual polarity being very much less.. It appears probable in terms of our present ideas of molecular structure that the electrons not directly held in the bonds between carbon and carbon and between carbon and hydrogen are quantized in respect to the field of the molecule as a whole. For each atom the direction of this resultant field is a line drawn through the center of the atom and the center of the ring. A pair of electrons rotating about this line might be thought of as binding one atom to all the other atoms of the ring, especially those in the ortho and para positions, as indicated in the diagram.

It is not especially profitable to speculate in terms of hypothetical benzene models; still, we believe that attempts to explain these orienting effects should be based upon some such electronic picture. In the above model unsubstituted benzene would be very nearly non-polar as on an average the three pairs of unshared electrons would be distributed equally among the six carbons. The substitution of a polar group would upset this balance. If the group is negative, the carbons in the ortho and para positions become slightly more negative. If the group is positive, the carbon atoms in the meta positions become relatively negative.

It is then only necessary to assume that the hydrogen ion is more readily displaced by the positive ion of the oxidizing agent from its electron pair on the negative carbon than from the pair on the positive carbon. Whether this is a matter of energy or of rate, depending upon the ease of activation, is not easily determined. The fact that varying amounts of all of the products are obtained seems to indicate that the rate of some step in the process is the determinative factor and that the ratio of the quantities of the products formed is not a good measure of their relative energies of formation.

Summary

A semi-quantitative measure of the polarity of a group attached to the benzene ring has been proposed which correlates the directing influence of various substituents. The polarity is discussed in terms of the electronic structure of benzene.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE PENNSYLVANIA STATE COLLEGE]

ELECTROMETRIC STUDIES ON THE 2-HYDROXYNAPHTHALENE SULFONIC ACIDS. PREPARATION OF PURE 2-HYDROXYNAPHTHALENE-6-SULFONIC ACID

BY KARL H. ENGEL AND A. WITT HUTCHISON

RECEIVED JUNE 7, 1929 PUBLISHED JANUARY 8, 1930

The purpose of the investigation was to study the neutralization curves, as obtained by electrometric titrations, of the 2-hydroxynaphthalenesulfonic acids in order to characterize them as acids and to determine especially the effect on the second dissociation constant of the position of the sulfonic acid group.

Preparation of Pure 2-Hydroxynaphthalene-6-sulfonic Acid.—In the study of this acid an especially pure material was desired. Though the preparation of metallic salts of the acid in a pure state may be accomplished by repeated recrystallization from their solutions, this cannot be done with the free acid because of its extreme solubility in water, alcohol, acetone, ether, etc.

It was found that the free acid may be precipitated from its aqueous solution by the addition of hydrogen chloride. This permitted a complete separation of the acid from excess sulfuric acid remaining in the sulfonation mass and from any isomeric compounds that may have been formed.

Schaeffer[1] first prepared the free acid from the lead salt by means of hydrogen sulfide. He obtained a crystalline compound which, when dried over concentrated sulfuric acid, melted at 125°. Later Ebert and Merz[2] used the same method of isolation and found a melting point of 122° but accepted Schaeffer's higher value as the correct one. Analyses of the compounds were not given in either case.

Preparation of the Free Acid from Hydrogen Chloride Solutions.—A mixture of 100 g. of 2-hydroxynaphthalene (Merck's resublimed) and 100 g. of sulfuric acid (100%) was stirred for seventy-five minutes at a temperature of 85°. The sulfonation mass, which had begun to solidify, was poured into a mixture of 500 g. of ice and water.

An aliquot portion of the solution was made alkaline with sodium carbonate and titrated with a standard solution of 1-diazo-2-methylbenzene hydrochloride. It was found that the solution contained 70% of the theoretically possible amount of the 2-hydroxynaphthalene-6-sulfonic acid.

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[1] Schaeffer, *Ann.*, 152, 296 (1869).

[2] Ebert and Merz, *Ber.*, 9, 609 (1876).

Traces of insoluble substances were removed by filtration from the solution of the sulfonation mass. The filtered solution was saturated with dry hydrogen chloride and a crystalline precipitate of the 2-hydroxynaphthalene-6-sulfonic acid appeared. Previous tests had shown that neither the isomeric 2-hydroxynaphthalene-8-sulfonic acid, nor the two 2-hydroxynaphthalenedisulfonic acids, 3,6- and 6,8-, which might have been formed during the sulfonation, could be precipitated in this way. The crystals were removed from the mother liquor by filtration and washed with hydrochloric acid (30%). They were redissolved in water and reprecipitated with hydrogen chloride until, after four such recrystallizations, a test with barium chloride showed the absence of sulfuric acid.

Analytical.—The purified crystals were allowed to stand for four weeks in a desiccator over potassium hydroxide sticks (Baker's Analyzed). A sample tested at this time with silver nitrate solution showed the absence of chloride ions.

Anal. Calcd. for $C_{10}H_6OH{\cdot}SO_3H{\cdot}2H_2O$: S, 12.32. Found: S, 12.23.

Melting point determinations were made by means of capillary tubes in a bath of sulfuric acid. The dihydrate melted sharply and without apparent decomposition at 118° corr. The dihydrate was stable at the water vapor tension of air at room temperatures. When placed in a desiccator over concentrated sulfuric acid or phosphorus pentoxide at 20°, a loss in weight corresponding to one mole of water occurred.

Anal. Loss calcd. for one mole of H_2O: 6.915%. Found over P_2O_5, 6.96%; over H_2SO_4, 6.92%. Samples regained their original weights when exposed to the air. The monohydrate melted sharply without decomposition at 129° corr.

A sample of the dihydrate when dried over phosphorus pentoxide in an atmosphere of dry nitrogen at 65° showed a loss corresponding to two moles of water.

Anal. Loss calcd. for two moles of H_2O: 13.83%. Found: 13.79%.

Samples regained their original weights when exposed to the air. The anhydrous acid melted sharply without decomposition at 167° corr.

It should be noted that the melting point of 125° given by Schaeffer agrees best with the value the authors have found for the monohydrate. Undoubtedly this was the compound he had prepared since he had dried the acid over concentrated sulfuric acid.

Materials and Apparatus.—The potassium salt of the 2-hydroxynaphthalene-6-sulfonic acid was prepared as suggested by Schaeffer.[1] The potassium salt of the 2-hydroxynaphthalene-1-sulfonic acid was prepared according to the method of Nietzki.[3] The 2-hydroxynaphthalene-6-sulfonic acid was prepared as described above.

The standard sodium hydroxide solution used in the titrations was prepared free from carbonates by diluting the required amount of a saturated sodium hydroxide solution with recently boiled distilled water. Fused benzoic acid was used as a standard.

The materials used in the calomel cells were reagents prepared by Leeds and Northrup Company especially for electromotive force measurements.

Experimental.—Fifteen-cc. portions of 0.1 molar solutions of the acids were titrated with 0.1 molar sodium hydroxide solution. The progress of the titrations was followed by measuring potential differences between a hydrogen electrode and a saturated calomel half-cell by means of a Leeds and Northrup Type K potentiometer. A suspended coil galvanometer with a sensitivity of 126 megohms was used as a null point instrument.

Data and Calculations.—The data obtained are listed in the tables. PH values were calculated from the equation.

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[3] Nietzki, Ber., 15, 305 (1882).

$$\frac{E(\text{obs.}) - E(\text{calcd.})}{0.00019837\ T} = \log \frac{1}{(\text{H})} = P_{\text{H}}$$

Values for pK and, from these, values for the usual dissociation constants were obtained from the equation

$$pK = P_{\text{H}} + \log \frac{\text{moles acid—moles base}}{\text{moles salt}}$$

as suggested by Clark.[4]

TABLE I

TITRATION OF 15 CC. OF 0.1 M SOLUTION OF THE POTASSIUM SALT OF 2-HYDROXYNAPHTHALENE-1-SULFONIC ACID WITH 0.1 N SODIUM HYDROXIDE

Temperature, 22 ± 0.5"; E, calcd. at 22°, 0.2480 volt

NaOH, cc.	Volt	Pa	$\text{Log}\ \frac{\text{moles acid—moles base}}{\text{moles salt}}$	pK	$K \times 10^{11}$	NaOH, cc.	Volt	P_{H}
0.0	0.6455	6.80				11.16	0.9071	11.26
.1	.7691	8.90				12.18	.9123	11.35
.3	.7987	9.42				13.20	.9167	11.43
.6	.8122	9.64				14.21	.9209	11.50
1.0	.8269	9.89				15.22	.9242	11.57
2.0	.8456	10.22				16.23	.9277	11.61
3.05	.8572	10.41				17.25	.9307	11.66
4.06	.8657	10.58				18.25	.9341	11.68
5.08	.8741	10.70	0.29	10.99	1.02	22.32	.9444	11.91
6.09	.8802	10.80	.17	10.97	1.08			
7.11	.8866	10.91	.05	10.96	1.11			
8.12	.8919	11.01	9.93–10	10.94	1.15			
9.14	.8976	11.11	9.81–10	10.92	1.21			
10.15	.9032	11.19	9.68–10	10.87	1.35			

These values have been plotted in the curve of Fig. 1.

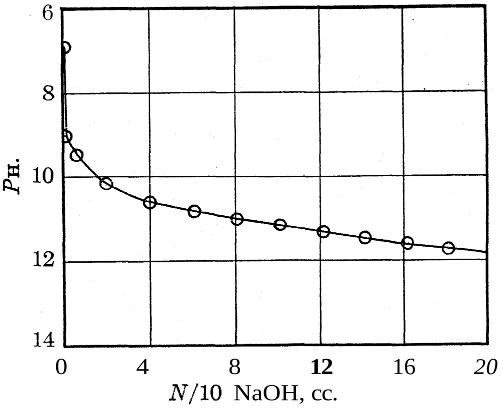

Fig. 1.—Titration of 15 cc. of $N/10$ potassium salt of 2-hydroxynaphthalene-1-sulfonic acid.

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[4] Clark, "The Determination of Hydrogen Ions," The Williams and Wilkins Co., Baltimore, 1923.

Table II

Titration of 15 Cc. of 0.1 *M* Solution of the Potassium Salt of 2-Hydroxynaphthalene-6-Sulfonic Acid with 0.1 *N* Sodium Hydroxide

Temperature, 18° ± 0.5°; E, calcd. at 18°, 0.2506 volt

NaOH, cc.	Volt	PH	Log $\frac{\text{moles acid}-\text{moles base}}{\text{moles salt}}$	pK	K X 10^9	NaOH, cc.	Volt	PH
0.0	0.4945	3.98				13.65	0.8204	9.87
.1	.6147	4.23				14.21	.8287	10.01
.2	.6597	6.31				14.71	.8416	10.24
1.0	.7030	7.83				14.82	.8440	10.28
2.0	.7222	8.17				15.01	.8504	10.39
3.05	.7329	8.35				15.22	.8589	10.53
4.06	.7430	8.53				15.42	.8604	10.66
5.08	.7502	8.65	0.29	8.95	1.14	15.62	.8753	10.82
6.09	.7578	8.79	.17	8.95	1.12	15.83	.8841	10.97
7.11	.7650	8.91	.05	8.96	1.11	16.04	.8893	11.07
7.62	.7687	8.98	9.99–10	8.96	1.11	16.24	.8967	11.20
8.12	.7730	9.05	9.93–10	8.98	1.05	16.64	.9063	11.40
9.14	.7798	9.17	9.81–10	8.98	1.05	17.05	.9130	11.49
10.15	.7865	9.28	9.68–10	8.96	1.10	18.25	.9266	11.70
11.16	.7941	9.41				19.27	.9329	11.83
12.18	.8020	9.55				20.30	.9385	11.92
13.20	.8130	9.74				22.33	.9459	12.06

These values have been plotted in the curve of Fig. 2.

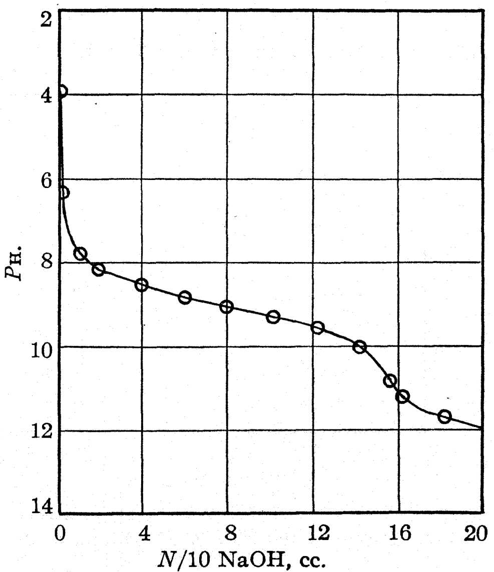

Fig. 2.—Titration of 15 cc. of *M*/10 potassium salt of 2-hydroxynaphthalene-6-sulfonic acid.

TABLE III

TITRATION OF 15 CC. OF 0.01 *M* SOLUTION OF 2-HYDROXYNAPHTHALENE-6-SULFONIC ACID WITH 0.1 N SODIUM HYDROXIDE SOLUTION

Temperature, 17 ± 0.5°; *E* calcd. at 17°, 0.2513 volt

NaOH, cc.	Volt	P_H	Log $\frac{\text{moles acid—moles base}}{\text{moles salt}}$	pK	K × 10^2
0.0	0.3139	1.09			
.5	.3141	1.09			
1.0	.3144	1.10			
1.5	.3153	1.12			
2.0	.3172	1.15			
3.05	.3193	1.19			
4.06	.3226	1.24			
5.08	.3258	1.30	0.29	1.59	2.59
6.09	.3331	1.42	.17	1.59	2.59
7.11	.3361	1.47	.05	1.52	3.03
7.62	.3377	1.50	9.99-10	1.48	3.25
8.12	.3406	1.55	9.93-10	1.48	3.25
9.14	.3440	1.61	9.81-10	1.42	3.81
10.15	.3480	1.68	9.68-10	1.36	4.37
11.16	.3543	1.79			
11.60	.3591	1.92			
12.18	.3637	1.95			
13.20	.3769	2.18			
13.65	.3861	2.35			
14.21	.4030	2.64			
14.51	.4217	2.96			
14.72	.4544	3.55			
14.91	.6182	6.41			
15.22	.6759	7.38			
15.62	.6964	7.27			
16.24	.7152	8.06			
17.25	.7317	8.39			
18.26	.7425	8.54			
19.28	.7506	8.68			*K* × 10^9
20.30	.7573	8.80	0.26	9.06	0.87
21.31	.7644	8.92	.13	9.06	.87
22.33	.7713	9.04	.02	9.06	.87
23.34	.7775	9.15	9.90-10	9.05	.89
24.36	.7846	9.27	9.78-10	9.05	.89
25.37	.7906	9.37	9.65-10	9.02	.95
26.35	.7985	9.51	9.50-10	9.01	.97
27.40	.8074	9.67	9.32-10	8.99	1.00
28.41	.8201	9.88			
29.44	.8351	10.15			
29.64	.8414	10.26			
29.84	.8472	10.36			
30.04	.8544	10.49			
30.25	.8622	10.62			
30.45	.8717	10.78			
30.65	.8793	10.92			

TABLE III *(Concluded)*

NaOH cc.	Volt	PH
30.85	0.8892	11.09
31.15	.8973	11.23
31.45	.9056	11.36
31.75	.9111	11.47
32.04	.9155	11.53
33.49	.9311	11.81
34.49	.9370	11.92
35.50	.9414	12.01
36.50	.9451	12.05

These values have been plotted in the curve of Fig. 3.

Discussion of Results.—The value of 1.1×10^{-11} determined for the dissociation constant of the hydroxy group of the 2-hydroxynaphthalene-1-sulfonic acid shows it to be an exceedingly weak acid. This is evident from the curve (Fig. 1) in which no break appears at the end-point of the titration. It is perhaps of interest to note that the value assigned to the constant for phenol is **1.3** $\times 10^{-10}$.[5]

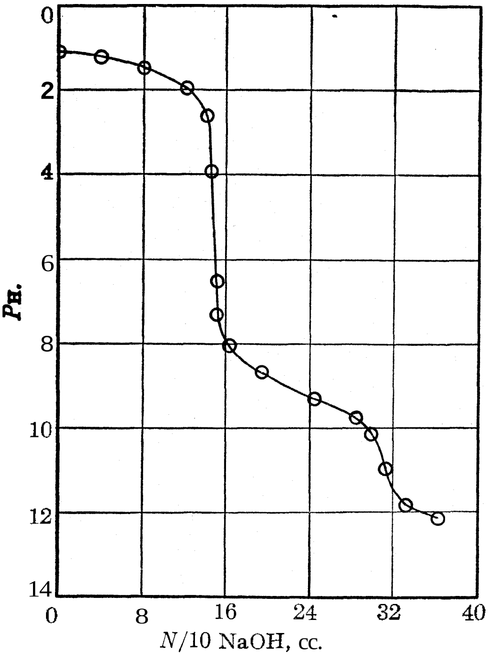

Fig. 3.—Titration of 15 cc. of $M/10$ 2-hydroxynaphthalene-6-sulfonic acid.

In the case of the constant for the hydroxy group of the 2-hydroxy-naphthalene-6-sulfonic acid the value 1×10^{-9} obtained both from the titration of the free acid and from that of its potassium salt is larger. Inspection of the curves (Fig. 2 and Fig. 3) shows that a definite break does occur at the end of the titration. It may be classed with the weak acids such as hydrogen sulfide, $K = 5.7 \times 10^{-8}$, or hydrocyanic acid, $K = 7.2 \times 10^{-10}$.[6] The break occurring in the curve of this acid makes possible its quantitative estimation in the presence of the 2-hydroxynaphthalene-1-sulfonic acid or of neutral salts.

The value of **3.3** $\times 10^{-2}$ found for the first dissociation constant of the 2-hydroxynaphthalene-6-sulfonic acid places it with the fairly strong

[5] Clark, Ref. 4, Appendix.

[6] Kolthoff and Furman, "Potentiometric Titrations," John Wiley and Sons, Inc., New York, **1926,** Tables.

acids, the value for the second hydrogen of sulfuric acid being 3×10^{-2}; for the first constant of oxalic acid, 3.8×10^{-2}.[6] The very sharp break occurring at the end-point of the curve of the free acid (Fig. 3) lends itself well to the quantitative estimation of the acid.

Summary

1. 2-Hydroxynaphthalene-6-sulfonic acid has been purified by recrystallization of the acid from aqueous solutions by means of the addition of hydrogen chloride. The identity of a monohydrate and a dihydrate has been established. Melting points for these three compounds have been determined.

2. The 2-hydroxynaphthalene sulfonic acids have been studied electrometrically and values determined for their acid dissociation constants. The nature of the curve obtained for the 2-hydroxynaphthalene-6-sulfonic acid shows that the quantitative estimation of the acid or of its salts might be possible in the presence of the isomeric 2-hydroxynaphthalene-1-sulfonic acid, or of neutral salts.

STATE COLLEGE, PENNSYLVANIA

[COMMUNICATION FROM THE DEPARTMENT OF CHEMISTRY, SMITH COLLEGE]

RESEARCHES ON CYCLIC ACETALS. I. FORMATION OF CYCLIC ACETALS OF 4,5-DIHYDROXY-2,6-OCTADIENE[1]

BY C. PAULINE BURT AND FRANCES HOWLAND

RECEIVED JUNE 18, 1929 PUBLISHED JANUARY 8, 1930

The tendencies toward formation of cyclic acetals have been investigated by Hibbert and co-workers.[2] In the majority of these investigations both the aldehyde and the glycol used were of the saturated type. More recently[3] work has been published on the tendencies of unsaturated glycols. The present investigation deals with a saturated glycol to form acetals with both the saturated and unsaturated type of aldehyde.

Experiments were carried out on the condensation of 4,5-dihydroxy-2,6-octadiene (dipropenyl glycol), $CH_3CH{=}CHCHOHCHOHCH{=}CHCH_3$, with acetaldehyde, paraldehyde, propionaldehyde, butyraldehyde, heptaldehyde, acetone, benzaldehyde, crotonaldehyde, cinnamaldehyde and chloral, using sulfuric acid as a catalyst. The yields of cyclic acetals obtained were taken as a basis of comparison for the tendencies of the aldehydes toward cyclic acetal formation.

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[1] This paper is constructed from a dissertation submitted in partial fulfilment of the requirements for the degree of Master of Arts at Smith College.

[2] 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).

[3] Hibbert, Houghton and Taylor, ibid., 51, 611 (1929).

The saturated carbonyl derivatives, acetaldehyde, paraldehyde, acetone, propionaldehyde, butyraldehyde and heptaldehyde all readily formed acetals of dipropenyl glycol with yields of 90, 83, 71, 90, 92 and 85%, respectively, acetaldehyde and paraldehyde forming the same acetal. Hibbert[4] has shown that acetaldehyde, butyraldehyde and heptaldehyde form acetals of ethylene glycol with yields of 87, 50 and 50%, respectively. It can, therefore, be concluded that unsaturation of the type in dipropenyl glycol does not decrease the tendency toward cyclic acetal formation, but instead seems to increase such a tendency. In attempting to condense chloral with dipropenyl glycol, a mixture of products was obtained but none could be identified as the acetal. It should not be concluded, however, that a cyclic acetal of chloral cannot be formed. Reaction apparently took place in all cases, but resulted in the original or resinous substances when attempts were made to isolate the products.

According to Hibbert,[3] substitution of hydrogen by chlorine atoms in the aldehyde residue of saturated aldehydes results in the formation of acetals of ethylene glycol in two cases. β-Phenyl-α,β-dichloropropylidene ethylene glycol was formed with a yield of 37%, and dichlorobutylidene ethylene glycol was formed with a yield of 50%. Experiments are now in progress on the condensation of several other saturated chloroaldehydes with dipropenyl glycol.

Negative results were also obtained when benzaldehyde was used with dipropenyl glycol. It has been shown that benzaldehyde with ethylene glycol[4] gives a yield of 80–85% of the acetal. The tendency of dipropenyl glycol to form an acetal with benzaldehyde is, therefore, much less than in the case of ethylene glycol.

The unsaturated aldehydes, crotonaldehyde and cinnamaldehyde, also showed little tendency to form the acetals of dipropenyl glycol; this is in agreement with the results of Hibbert,[3] who showed that the amount of reaction of ethylene glycol with these aldehydes was negligible.

Experimental Part

In all cases one part of dipropenyl glycol and about twice the calculated quantity of the aldehyde or ketone were heated in a bath at about 70° for four hours with a few drops (4–6) of 40% sulfuric acid for each tenth mole of the glycol used. At the end of the reacting period an equal volume of ether and sufficient 5% sodium carbonate solution for neutralization were added. The ether solution was washed, dried and distilled. Acetals were obtained as slightly yellow oils in high yield (71–92%) from acetaldehyde, paraldehyde, propionaldehyde, butyraldehyde, heptaldehyde and acetone, as shown in the table, while no product could be obtained when using crotonaldehyde, cinnamaldehydc, chloral and benzaldehyde.

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[4] Hibbert, THIS JOURNAL, 46, 1286 (1924).

TABLE OF RESULTS

CONDENSATION PRODUCTS OF DIPROPENYL GLYCOL WITH VARIOUS HYDROCARBON CARBONYL DERIVATIVES

	Carbonyl deriv.	B. p., °C.	Acetal, -dipropenyl glycol	B. p., °C.	Press., mm.
1	Acetaldehyde	21	Ethylidene	88–89	20
2	Paraldehyde	124	Same results as with acetaldehyde		
3	Propionaldehyde	48.8	Propylidene	99–100.5	21
4	Butyraldehyde	73–74	Butylidene	104–105	15
5	Heptaldehyde	153–155	Heptylidene	129–131	4
6	Acetone	56.5	Acetone	72–75	8

	Analysis, %			
	Calcd.		Found	
No.	C	H	C	H
1	71.37	9.59	70.97, 71.20	10.16, 10.31
2	...	...	....	....
3	72.47	9.96	72.02, 72.07	10.58, 10.51
4	73.41	10.27	73.10, 72.75	11.08, 10.92
5	75.56	11.00	75.29, 75.67	11.09, 11.40
6	72.47	9.96	72.57, 72.37	10.25, 9.97

Summary

1. A comparison has been made of the tendency of saturated, chloro-saturated and unsaturated aldehydes to form acetals of dipropenyl glycol.

2. The saturated aliphatic carbonyl derivatives, acetaldehyde, paraldehyde, propionaldehyde, butyraldehyde, heptaldehyde and acetone showed a marked tendency to form acetals with yields of 90, 83, 90, 92, 85 and 71%, respectively, indicating that the length of the hydrocarbon chain of the carbonyl compound has practically no effect on the yield. The saturated chloro derivative, chloral, does not give an acetal as a product. The acetal of benzaldehyde was not formed under the conditions used.

3. The unsaturated aldehydes, cinnamaldehyde and crotonaldehyde show practically no tendency to form acetals.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT DUKE UNIVERSITY]

MIXED BENZOINS. I

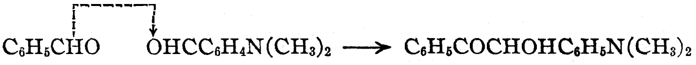
BY JOHANNES S. BUCK AND WALTER S. IDE

RECEIVED JUNE 21, 1929 PUBLISHED JANUARY 8, 1930

By mixed benzoins is understood unsymmetrical benzoins, that is, benzoins formed from two different aldehydes, or, in other words, containing different substituents in the two rings. A considerable amount of theory has been written on simple benzoin formation but there is little of practical value. Staudinger[1] is one of the few authors to speculate on the question of mixed benzoins. To support his views he prepared two mixed benzoins. Fischer[2] also prepared two mixed benzoins but made no speculations. These four compounds, together with one prepared by Ekecrantz and Ahlqvist,[3] represent the total number of mixed benzoins prepared heretofore by the condensation method.

Staudinger regards benzoin formation as due to the migration of a hydrogen atom from one aldehyde group to the carbonyl group of the other aldehyde, and hence he divides aldehydes into two main types—Type A having a reactive carbonyl group and a non-mobile hydrogen atom, and Type B, which has a mobile hydrogen atom but does not possess an active carbonyl group. The criterion for Type A is not stated; presumably it is the ability of the aldehyde to react with the usual aldehyde reagents. Type B is characterized by the rate of auto-oxidation. There are necessarily many intermediate aldehydes possessing both an active carbonyl group and a mobile hydrogen atom (although in varying degrees). Benzaldehyde, which forms a benzoin, belongs to this class.

On Staudinger's views the aldehydes of Type B donate the hydrogen atom and hence the nucleus of this aldehyde appears in the resulting benzoin next to the carbonyl group of the CHOH-CO chain. This may be illustrated by an example.



$$C_6H_5CHO \quad OHCC_6H_4N(CH_3)_2 \longrightarrow C_6H_5COCHOHC_6H_5N(CH_3)_2$$

The method used by Staudinger was to heat two selected aldehydes, one each of Types A and B, in alcoholic potassium cyanide solution. Clearly, since neither aldehyde can form its own simple benzoin, and since only one mixed benzoin can be formed, the method will give excellent yields, provided always that the aldehydes are typical.

The case of the majority of aldehydes, which are not exclusively of either type, presents serious difficulties, since both simple benzoins and two

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[1] Staudinger, Ber., 46, 3535 (1913).

[2] Fischer, Ann., 211, 214 (1882).

[3] Ekecrantz and Ahlqvist, *Arkiv Kemi, Mineral. Geol.*, 3, Nr. 13, 26 S (1908–1910).

mixed benzoins may all be formed simultaneously. Their separation would then be a matter of chance depending on their relative solubilities. Fischer's two mixed benzoins were evidently obtained only because of their favorable solubilities.

The authors sought to make the production of mixed benzoins a more general process by considering the reaction from a dynamic point of view. They consider that the speed of formation of the simple benzoin is a rough index either of the mobility of the hydrogen atom or of the reactivity of the carbonyl group (without, at this stage, making any distinction). Aldehydes forming simple benzoins, and therefore possessing to some extent both a reactive carbonyl group and mobile hydrogen atom, are henceforth referred to as Group I. Aldehydes which form no simple benzoin, and therefore possess only a mobile hydrogen atom or a reactive carbonyl group (but not both), are classed as Group 2. The speed of formation of a simple benzoin may be roughly indicated by primes, thus $1''''$ signifies that the aldehyde forms a simple benzoin very rapidly. The relation between Staudinger's and the authors' grouping is simply that Group 1 possesses in varying degree the properties of both Types A and B. Group 2 is either of Type A or of Type B.

By adding the aldehydes at different speeds to the reaction mixture and by varying the time of heating, the authors have been able to isolate a number of new mixed benzoins and to improve the yields of some already known. Doubtless a considerable number of others could be prepared by similar methods. The rates of addition and the times of heating have to be determined by trial, since data on the speed of formation of benzoins are practically non-existent.

To illustrate the argument, consider one mole of an aldehyde of Group 2 in boiling alcoholic potassium cyanide solution. No reaction will take place. If now one mole of an aldehyde of Group 1 is run in at such a rate that it does not accumulate in the reaction mixture, it will form little of its own simple benzoin, being at high dilution, but will (on mass action considerations) form large amounts of one mixed benzoin. The formation of one mixed benzoin is also necessitated by the aldehyde of Group 2 possessing only a mobile hydrogen atom or a reactive carbonyl group, but not both.

Three other cases remain to be considered. If both aldehydes are of Group 2, but one of Type A and the other of Type B, a single mixed benzoin will be formed under any conditions. This is Staudinger's case. If both aldehydes are of Group 2 and both of Type A or both of Type B, then no mixed, or simple, benzoin will be formed. Lastly, as is usually the case, if both aldehydes are of Group I, then necessarily four products will be formed, two simple and two mixed benzoins. However, by adding both aldehydes, say $1'$ and $1'''$ at such rates that aldehyde $1'$ is always present in relatively great excess to $1'''$ (but usually at small concentration) and adjusting the rate of addition so that neither aldehyde accumulates, the formation of the simple benzoin from 1" is largely suppressed, while the simple benzoin from 1' (slow aldehyde) has not had time to form to any extent. The conditions then favor the formation of the mixed benzoins, but the fact that aldehyde 1' must nearly approach either Type A or B will cause one mixed benzoin to preponderate. The present paper largely deals with reactions of this type. In the limiting case, where both aldehydes are of Group 1 and have about the same speeds of formation of simple benzoins, both simple and mixed benzoins are necessarily formed, whatever conditions are used. In one case of this type the authors have succeeded in isolating both of the mixed benzoins.

The position of the CHOH group in the mixed benzoin could only be definitely settled by synthesizing the compound in some other way which would leave no doubt as to its position. However, as previously explained, when one aldehyde belongs to Type A or to Type B, the position of the CHOH group can be assigned with fair certainty, for it will be next to the nucleus of the Type A aldehyde or furthest from the nucleus of the Type B aldehyde. The possibility of assigning a correct structure when both aldehydes belong to Group 1 depends upon which type (A or B) the aldehydes are most nearly related to.

It has been shown by Lachman[4] that in the ordinary benzoin reaction a number of side-products are formed. The amount, however, is not serious if the heating be not too prolonged. In the present work the side-products were avoided as much as possible, but they undoubtedly render the separation of mixed benzoin more difficult.

Nomenclature.—In the literature mixed benzoins are named from the two aldehydes, with the termination -oin. The authors suggest placing this termination after the aldehyde with the reactive carbonyl group, or, which is the same thing, after the aldehyde whose CHO becomes CHOH. Thus, $CH_2O_2C_6H_3COCHOHC_6H_5$ is piperbenzoin and $CH_2O_2C_6H_3CHOHCOC_6H_5$ is benzpiperoin. If the structure is doubtful a query mark is placed after the name.

Experimental

The experimental procedure, in general, is very simple. A three-necked flask contains the alcoholic potassium cyanide solution, which is kept boiling briskly on a steam-bath. Two burets and a reflux condenser are fitted to the three necks. The time of addition and the amount of one aldehyde first added have been determined by trial from a number of experiments. In general both aldehydes were added at the same rate after the preparation was begun. The amounts of water, alcohol and potassium cyanide were also varied—the optimum values are given.

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[4] Lachman, THIS JOURNAL, 46, 709 (1924).

Furo-*p*-dimethylaminobenzoin.—To a boiling solution of 7.5 g. of *p*-dimethylaminobenzaldehyde and 3.0 g. of potassium cyanide in 55 cc. of 65% alcohol was added 5.0 g. of furfural over a period of forty-five minutes. On standing overnight a crystalline product separated. After recrystallization from alcohol the compound forms buff plates melting at 168° and is very soluble in chloroform, moderately soluble in benzene and alcohol and slightly soluble in ether and ligroin; yield, 30%.

Anal. Calcd. for $C_{14}H_{15}O_3N$: N, 5.71. Found: N, 5.99.

***o*-Chloro-*p*-dimethylaminobenzoin.**—A solution of 7.5 g. of *p*-dimethylaminobenzaldehyde, 7.5 g. of o-chlorobenzaldehyde and 2.0 g. of potassium cyanide in 45 cc. of 65% alcohol was refluxed for one hour. On addition of ice water, a solid separated and was recrystallized from alcohol; yield, 36%.

It forms white needles melting at 166° and is very soluble in chloroform, moderately soluble in benzene and alcohol, slightly soluble in ligroin and ether.

Anal. Calcd. for $C_{16}H_{16}O_2ClN$: N, 4.83. Found (Kjeldahl): N, 4.77, 4.69.

***m*-Bromo-*p*-dimethylaminobenzoin.**—This compound was prepared by heating a solution of 7.5 g. of p-dimethylaminobenzaldehyde, 9.0 g. of m-bromobenzaldehyde and 3.0 g. of potassium cyanide in 45 cc. of 65% alcohol for an hour. On adding ice water a solid product separated and was recrystallized from alcohol; yield, 50%. It forms buff prisms melting at 145° and is very soluble in chloroform, moderately soluble in alcohol and benzene and slightly soluble in ether and ligroin. Analyses were made by the Kjeldahl method.

Anal. Calcd. for $C_{16}H_{16}O_2NBr$: N, 4.19. Found: N, 4.01, 4.13.

Benzpiperoin.—Fifteen grams of piperonal in saturated alcoholic solution are added during one and three-fourths hours to a boiling solution of 10.6 g. of benzaldehyde in 120 cc. of 50% alcohol containing 5.0 g. of potassium cyanide. The oil which separated on cooling was removed and dissolved in alcohol. The product crystallized in a few hours and was recrystallized from alcohol; yield, 28%. It forms white needles, m. p. 120°, very soluble in chloroform, moderately soluble in alcohol, ether, ligroin and benzene.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.30; H, 4.70. Found: C, 69.93; H, 4.97.

Piperbenzoin.—The mother liquors from the preparation of benzpiperoin sometimes deposit, on standing for several days, an isomer, melting at 112°, in a yield of about 16%. It forms white needles, rather more soluble than benzpiperoin, especially in ether.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.30; H, 4.70. Found: C, 70.06; H, 4.87.

Benz-m-bromobenzoin (?).—This compound is best prepared by dissolving 18.5 g. of m-bromobenzaldehyde in 140 cc. of 50% alcohol containing 5.0 g. of potassium cyanide and boiling for two hours while 15.0 g. of benzaldehyde is run in. An oil separated on cooling and was sludged with benzene. The crystals which formed were recrystallized from alcohol; yield, 32%.

Benz-*m*-bromobenzoin forms white prisms, m. p. 129–130°, very soluble in chloroform and moderately soluble in benzene, alcohol, ether and ligroin.

Anal. Calcd. for $C_{14}H_{11}O_2Br$: C, 57.73; H, 3.77. Found: C, 58.00; H, 4.08.

Piper-m-bromobenzoin (?).—Eighteen and one-half grams of m-bromobenzaldehyde dissolved in 160 cc. of 50% alcohol containing 5.0 g. of potassium cyanide was treated over one and a half hours with 15.0 g. of piperonal in saturated alcohol solution. The mixture was kept boiling and the piperonal was added at a steady rate. On cooling, the oil which separated was removed and kept in a refrigerator, where it gradually crystallized. The product was recrystallized from ether and then alcohol; yield, 33%.

Piper-m-bromobenzoin forms white needles, m. p. 106°, very soluble in benzene and chloroform, moderately soluble in ether, ligroin and alcohol.

Anal. Calcd. for $C_{15}H_{11}O_4Br$: C, 53.73; H, 3.28. Found: C, 53.68; H, 3.38.

Piper-o-chlorobenzoin (?).—Three and sixty-five one-hundredths grams of *o*-chlorobenzaldehyde was dissolved in 50 cc. of 50% alcohol containing 3.0 g. of potassium cyanide and the whole was boiled briskly; 3.75 g. of piperonal in saturated alcoholic solution was added at a steady rate over one and three-fourths hours. On cooling, an oil separated which was removed and sludged with ligroin. After twenty-four hours the crystalline product was filtered off and recrystallized from alcohol; yield, 50%.

Piper-o-chlorobenzoin forms white needles, m. p. 115°, very soluble in benzene and chloroform, moderately soluble in alcohol, ether and ligroin.

Anal. Calcd. for $C_{15}H_{11}O_4Cl$: C, 61.94; H, 3.78. Found: C, 61.84; H, 4.14.

Summary

By considering the reactivity of aldehydes in the simple benzoin reaction, a method has been worked out whereby mixed benzoins may be obtained from the large majority of aromatic aldehydes. Eight new mixed benzoins have been prepared by the method.

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

SUBSTITUTED PHENYLETHYLBARBITURIC ACIDS[1]

BY E. W. BOUSQUET AND ROGER ADAMS

RECEIVED JUNE 27, 1929 PUBLISHED JANUARY 8, 1930

Of the numerous 5,5-disubstituted barbituric acids that have been prepared and offered to the physician as hypnotics, the one which is of peculiar interest is the phenylethyl derivative.[2] This substance is generally accepted by the clinician as having, in addition to the usual soporific value, a specific sedative action toward epileptics, much more marked than appears in the various dialkylbarbituric acids. Phenylethylbarbituric acid (phenobarbital) is more toxic than most of the important dialkyl derivatives, though the ratio of effective dosage and toxicity is not so very different from that of barbital[3] itself. The phenylmethyl[4] and the phenylallyl[5] barbituric acids have also been prepared, but appear to be of less interest than the better-known phenylethyl derivative.

In spite of the importance of phenobarbital, derivatives containing substituents in the benzene ring, with the exception of the *p*-methoxyphenylethylbarbituric acid,[2] which was mentioned in the original patent, have never been prepared. Numerous investigators have obtained barbituric acid derivatives isomeric with phenylalkyl- or phenylallylbarbituric

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[1] This communication is an abstract of a portion of a thesis submitted by E. W. Bousquet in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] German Patent 249,722, *Friedländer*, XI, 928 (1912).

[3] Nielsen, Higgins and Spruth, *J. Pharmacol.*, 26, 271 (1925).

[4] U. S. Patent 1,025,526 (1912).

[5] U. S. Patent 1,056,793 (1912).

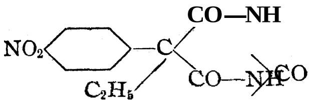
acid, such as benzylalkyl,[6] benzylallyl[7] or ethylphenethyl.[8] None, however, proved to be of any value. The dibenzyl-,[9] the 5,5-di-(*p*-hydroxyphenyl)-[10] and the 5,5-di-(3-methyl-4-hydroxyphenyl)-[10] barbituric acids have also been described and were shown to have no soporific effect.

This investigation had as its object the preparation of substituted phenylalkylbarbituric acids, in order, if possible, to obtain a compound with lower toxicity and possibly higher soporific value than phenobarbital.

The method commonly used for preparing phenylethylbarbituric acid is condensation of phenylacetic ester and oxalic ester to phenyloxalacetic ester, elimination of carbon monoxide by heating to give phenylmalonic ester, condensation with an alkyl halide to give phenylalkylmalonic esters and, finally, condensation to the corresponding barbituric acid. The application of this procedure is of questionable value on account of the difficulty of obtaining substituted phenylacetic esters, and also because such substitution products do not enter readily into the subsequent reactions. No directions were given in the original patent for preparing the *p*-methoxyphenylethylbarbituric acid but, presumably, the method just mentioned was the one used.

The procedure first attempted in this research was to nitrate phenylethylmalonic ester and to obtain through the nitro group a variety of substituted phenylethylmalonic esters which could be condensed in the usual way to the barbituric acids. Conditions were found for nitration which gave the p-nitro derivative in good yields. The position of the substituting group was proved by oxidation to p-nitrobenzoic acid. The nitro compound was reduced to the corresponding amino and the amino, in turn, further substituted or replaced. However, proper conditions were not found for the condensation of any of the substituted phenylethylmalonic esters to the corresponding barbituric acids.

Attention was next given to the nitration of phenylethylbarbituric acid itself. A very satisfactory yield of product was obtained (I), and through this substance a series of derivatives was produced: the amino, the bromo-amino, the acetamino, the bromo-acetamino, the nitro-acetamino, the nitroamino and the chloro. The nitro, the amino, the acetamino, the bromo-acetamino, the bromoamino, and the chloro derivatives were kindly tested for their soporific value and toxicity by H. C. Spruth of the Abbott Laboratories, for whose help the authors are grateful. With the exception of the chloro, each was



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[6] Dox and Yoder, THIS JOURNAL, 44, 1141 (1922); Shonle and Moment, *ibid.*, 45, 243 (1923).

[7] Johnson and Hill, Am. Chem. J., 46, 537 (1912).

[8] Dox, THIS JOURNAL, 46, 2843 (1924).

[9] Fischer and Dilthey, Ann., 335, 334 (1904).

[10] Dox, THIS JOURNAL, 45, 1811 (1923).

found to be less toxic than phenobarbital itself, but, as so frequently happens in the study of the relation between pharmacological action and chemical constitution in organic compounds, the substitution of these groups caused the hypnotic property to disappear entirely. The chloro compound possessed hypnotic power of almost the same order as the parent substance, phenobarbital, but was slightly more toxic.

Experimental

Preparation of the Substituted Aryl-alkyl-malonates

Methyl Ethyl *p*-Nitrophenylethylmalonate.—Fifteen grams of the pure methylethyl ester of phenylethylmalonic acid, b. p. 142–147" (5 mm.), was dissolved in 15 cc. of ice-cold concentrated sulfuric acid. The temperature of the ester–sulfuric acid mixture was brought down to −10° and a cold nitrating mixture consisting of 0.072 mole of fuming nitric acid (sp. gr. 1.50) in 5 cc. of concentrated sulfuric acid was added very slowly, while stirring and keeping the temperature of the reaction between −10 and 0°. Stirring was continued for two hours after the nitrating mixture had been added. The reaction mixture was added to ice-water mixture and the oily mass extracted with ether. After washing and drying, the solvent was removed and a crude yellow oil weighing 16 g. (90.4%) was obtained. Several runs using twice the molecular proportions of the above experiment gave consistent yields of 87.5% of the theoretical of purified product.

Oxidation of Methyl Ethyl *p*-Nitrophenylethylmalonate.—Five grams of the nitro ester was dissolved in 20 cc. of 95% alcohol and 3.5 g. of solid potassium hydroxide was added. After refluxing for two hours on the steam-bath, the alcohol was evaporated off, and a hot solution of 15 g. of potassium permanganate in 100 cc. of water was added all at once with stirring. The solution was allowed to stand for two hours and then filtered from the manganese dioxide. Upon acidification of the filtrate with concentrated hydrochloric acid, 0.5 g. of a white product precipitated. Two recrystallizations from dilute alcohol gave a product melting at 235–237° (uncorr.). Several mixed melting points containing various percentages of *p*-nitrobenzoic acid with the oxidation product showed no depression of the original melting point.

Methyl Ethyl *p*-Aminophenylethylmalonate.—A solution of 30 g. of methyl ethyl *p*-nitrophenylethylmalonate, b. p. 180–185° (4 mm.), in 50 cc. of 95% alcohol was reduced with hydrogen and 0.2 g. of platinum-oxide catalyst.[11] At 2–3 atm. pressure after half an hour, the theoretical amount of hydrogen had been absorbed, and the spent catalyst was filtered off and the alcohol evaporated. The resulting dark red oil amounted to 25 g. (92.7%). When pure it was a very viscous, heavy, yellow oil. Attempts to form a solid hydrochloride or benzoyl derivative were unsuccessful.

Methyl Ethyl *p*-Acetaminophenylethylmalonate.—Fifteen grams of the crude amino ester was slowly mixed with 17.5 g. of pure acetic anhydride. The reaction mixture was heated over the steam-bath for four hours and then distilled. The pure product was a very viscous, yellow oil. Crystallization could not be induced.

Methyl Ethyl *p*-Hydroxyphenylethylmalonate.—Fifteen grams of the crude amine was dissolved in a cold dilute acid mixture consisting of 20.5 g. of concentrated sulfuric acid and 15 g. of water. Twenty-eight grams of ice was then added to the sulfate. When cooled down to 0°, it was treated with a solution of 3.8 g. of sodium nitrite in 10 cc. of water, while maintaining the temperature between 0 and 5°. The diazonium mixture was then poured into a boiling solution of 35 cc. of concentrated sulfuric acid

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[11] Adams and Shriner, THIS JOURNAL, 45, 2171 (1923).

and 30 cc. of water and stirred until the evolution of gases had subsided. The black oily layer was extracted with ether and the ether extracts washed with 5% sodium hydroxide solution to take up the phenolic ester. The phenolic ester was then regenerated by treatment with dilute hydrochloric acid and extracted with ether. Six and one-half grams of a very viscous, yellow oil was obtained.

Methyl Ethyl *p*-Methoxyphenylethylmalonate.—Fifteen grams of freshly distilled phenolic ester was dissolved in a 20% excess of 5% sodium hydroxide solution and to this alkaline solution 8 g. of freshly distilled dimethyl sulfate was added with vigorous shaking, keeping the temperature below 60°. The reaction mixture was heated at 60–70° for an hour and when cool was extracted with ether, Ten and one-half grams of a lemon-yellow oil was obtained.

TABLE I

DERIVATIVES OF METHYL ETHYL PHENYLETHYLMALONATE

Methyl ethyl —ethylmalonate	B. p., °C.	Analyses Calcd., % C	H	Found, % C	H
p-Nitrophenyl	180–185 (4 mm.)	56.92	5.80	56.91	5.71
p-Aminophenyl	182–185 (4 mm.)	63.36	7.22	63.40	7.22
		(N, 5.28)		(N, 5.02)	
p-Acetaminophenyl	192–197 (3 mm)	62.50	6.89	62.23	6.82
p-Hydroxyphenyl	180–185 (4 mm.)	63.12	6.87	64.13	6.85
p-Methoxyphenyl	152–156 (4 mm.)	64.24	7.19	64.25	7.13

Preparation of Substituted Aryl-alkylbarbituric Acids

5-Nitrophenyl-5-ethylbarbituric Acid.—Five grams of phenylethylbarbituric acid, m. p. 169–170°, was added to 20 cc. of ice-cold concentrated sulfuric acid. A nitrating mixture of 1.1 cc. of fuming nitric acid (sp. gr. 1.50) in 5 cc. of concentrated sulfuric acid was added slowly to the rapidly stirred mixture, while maintaining the temperature between −10 and 3°. Stirring was continued for an hour after the nitrating mixture was added. The nitration mixture was added to 300 cc. of ice-water mixture and filtered when cold. The white precipitate was washed with water until almost neutral to litmus and then dried at 100°. Two crystallizations gave 2 g. of pure material. Recrystallizations of material in the mother liquors gave average yields of 60–65% of the pure product.

5-Aminophenyl-5-ethylbarbituric Acid.—Ten grams of the nitro compound, m. p. 276–277" (uncorr.), was suspended in 125 cc. of 95% ethyl alcohol with 0.2 g. of platinum-oxide catalyst. The reduction was carried out at 40–50° at a pressure of 2–3 atm., and the theoretical amount of hydrogen was absorbed in twenty to thirty minutes

5-Acetaminophenyl-5-ethylbarbituric Acid.—Nine grams of the amino compound was poured slowly into 11 g. of freshly distilled acetic anhydride, keeping the temperature below 50°. The hard, crystalline mass was heated at 70° for half an hour, after which 20 cc. of glacial acetic acid was added and the solution refluxed until a test portion with sodium nitrite solution and β-naphthol showed that acetylation was complete. The reaction was diluted with 100 cc. of water and filtered, washed and dried at 100°. Two recrystallizations gave 6 g. of pure product. It contained one molecule of water of crystallization.

5-(Bromo-acetaminopheny1)-5-ethylbarbituric Acid.—Two grams of the acetamino compound was brominated with 10% excess of dry bromine in 10 cc. of glacial acetic acid at 60–70°. Evolution of hydrogen bromide had ceased in an hour and the cold brominated product was precipitated by adding 50 cc. of cold water, filtered, washed and dried. Three recrystallizations gave pure material, 5-(Nitro-acetaminophenyl)-5-ethylbarbituric Acid.—Twenty cc. of concentrated sulfuric acid was cooled to −10° and 5 g. of acetamino compound was added with rapid stirring, keeping the temperature below 0°. A nitrating mixture containing 1.15 cc. (20% excess) of nitric acid (sp. gr. 1.42) and 5 cc. of concentrated sulfuric acid was then added, keeping the temperature between —10 and 3° during the addition. Stirring was continued for fifteen minutes after the nitrating agent had been added. The reaction mixture was poured into 150 cc. of ice water and a light yellow product separated out. The product, after two crystallizations was pure.

5-(Bromo-aminophenyl)-5-ethylbarbituric Acid.—Ten grams of the brominated acetamino compound was refluxed for five hours with 70 cc. of 95% alcohol and 30 cc. of 30% sulfuric acid. The alcohol was distilled off and just enough 10% sodium hydroxide solution was added to neutralize the sulfuric acid present.

5-(Nitro-aminophenyl)-5-ethylbarbituric Acid.—Fifteen grams of the nitrated product was refluxed for five hours with 150 cc. of 95% ethyl alcohol and 40 cc. of 20% sulfuric acid. The cold solution was filtered and 95.2% of the theoretical amount of fine yellow needles which did not melt below 320° was obtained. Purification was accomplished by taking up the product in a slight excess of cold 5% sodium hydroxide solution, filtering and precipitating by slow addition of dilute hydrochloric acid while stirring the solution rapidly. The precipitate was filtered, washed with alcohol and dried.

5-Chlorophenyl-5-ethylbarbituric Acid.—A solution of cuprous chloride was made by adding a mixture of 2.7 g. of sodium acid sulfite and 1.8 g. of solid sodium hydroxide in 20 cc. of water to a solution of 12.6 g. of copper sulfate and 2.3 g. of sodium chloride in 40 cc. of hot water. The white precipitate of cuprous chloride after filtration was treated with 8 cc. of concentrated hydrochloric acid and 40 cc. of water.

A diazonium salt solution was made by dissolving 10 g. of the amine in 35.5 cc. of concentrated hydrochloric acid, 20 cc. of water and 37 g. of ice. After cooling to 0°, a solution of 2.86 g. of pure sodium nitrite in 15 cc. of water was added to the amine hydrochloride. To the cuprous chloride solution was added as rapidly as possible the above diazonium salt solution, keeping the temperature between 0 and 5° for twenty minutes after addition of the solutions, when the reaction mixture was allowed to come to room temperature in the course of two hours. It was then heated to 60° for a short time.

The crude yellow product from 10 g. of the amine was washed thoroughly with 5% ammonium chloride solution, followed by water to remove all traces of insoluble copper salts; the yellow dry powder weighed 9.5 g. (83.5%) and melted with decomposition at 239–243° (uncorr.). The crude yellow powder after three recrystallizations from methyl alcohol, acetone and glacial acetic acid was pure.

TABLE II

DERIVATIVES OF PHENYLETHYLBARBITURIC ACID

( )-Phenyl-5-ethyl-barbituric acid	M. p., °C. (uncorr.)	Cryst. solvent	Needles	Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found
5-Nitro-	276–277	95% EtOH	White	51.96	51.75	4.05	4.03
5-Amino-	205–206	95% EtOH	White	58.26	57.83	5.30	5.33
5-Acetamino-[a]	147–148	70% EtOH	White	54.72	54.53	5.53	5.68
5-Bromo-acetamino-	291–292	Gl. HAc	White	Br, 21.73; found, 21.57			
5-Nitro-acetamino-	295–296	70% EtOH	Yellow	50.27	48.98	4.22	4.28
5-Bromo-amino-	253–255	60% EtOH	Yellow	Br, 24.57; found, 24.91			
5-Nitro-amino-	>320	Rppt. NaOH	Yellow	49.29	49.07	4.14	4.24
5-Chloro-	dec. 243–245	MeOH, HAc, acetone	Tan	Cl, 13.30; found, 12.81			

[a] Calcd.: H_2O, 5.86. Found: H_2O, 5.84.

Several attempts at replacing the amino group by hydroxyl were unsuccessful and only a reddish brown dye melting with decomposition between 260–270° was isolated but not identified.

Summary

1. 5-Phenyl-5-ethylbarbituric acid has been nitrated.

2. The following groups have been introduced into the phenyl ring through the nitro group: amino-, acetamino-, bromo-acetamino-, bromo-amino-, nitro-amino-, nitro-acetamino-, chloro-.

3. Methyl ethyl phenylethylmalonate has been nitrated and the nitro group shown to be in the para position in the benzene ring. In addition the following groups have been introduced into the phenyl ring of methyl ethyl phenylethylmalonate: 4-amino-, 4-hydroxy-, 4-acetamino-, 4-methoxy-.

4. None of the substituted phenylethylmalonates could be condensed with urea to form the corresponding barbituric acids.

5. Preliminary physiological tests which have been carried out on a majority of the 5,5-substituted phenylalkylbarbituric acids show that these compounds with the exception of the 4-chlorophenylethylbarbituric acid are inert. The sedative properties of the chloro derivative are of the same order as those of phenylethylbarbituric acid but the substance is slightly more toxic.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

CONDENSATION PRODUCTS OF AMINO-ARSANILIC AND ARSANWC ACIDS[1]

BY P. L. CRAMER WITH W. LEE LEWIS

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This paper is a continuation of the study[2] of condensation products of amino-arsanilic acid with 1,2-diketones to yield arsenated quinoxalines and with monocarbonyl compounds to form arsenated Schiff's bases. In the present study arsanilic acid as well as amino-arsanilic acid has been employed.

Glyoxal sodium bisulfite condenses with amino-arsanilic acid to give 6-arsono-quinoxaline-2,3-sodium bisulfite. This compound when treated with hydrochloric acid gives 6-arsono-quinoxaline, parent substance of this series.

Maltosone and lactosone, prepared according to the method of Emil

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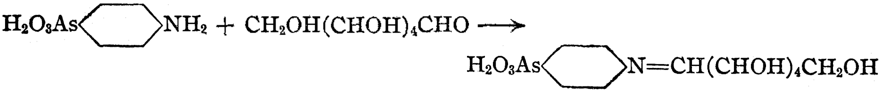
[1] This research was carried out under a grant from the Public Health Institute of Chicago. Some of the compounds are being studied for possible therapeutic value at the University of Wisconsin in the Department of Pharmacology.

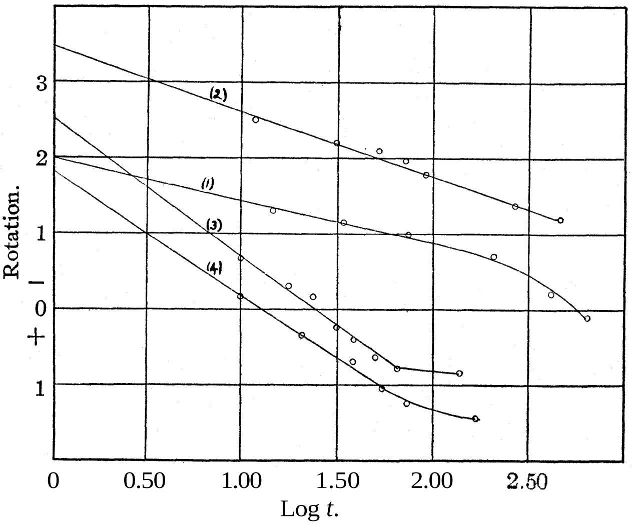
[2] W. Lee Lewis, P. L. Cramer and R. S. Bly, THIS JOURNAL, 46,2058 (1924).

Fischer,[3] condense with amino-arsanilic acid to give substituted quinoxalines. These compounds are readily hydrolyzed by water.

Aldoses condense with arsanilic acid to form Schiff bases containing an aromatic arsonic acid group and a carbohydrate residue. The reaction of glucose is typical of these reactions.



Similar products were obtained with mannose, galactose, arabinose and xylose. These compounds are also very soluble in water and readily hydrolyzed. The rotations of the sugars are inverted by the aromatic arsonic acid group. Due to the fact that these compounds are insoluble in organic solvents and decompose rapidly in water, no definite rotation data could be obtained. The data given indicate the degree and rate of hydrolysis.



Pig. 1.—Curves showing the rate of hydrolysis and the approximate initial rotations of **4-aldo-aminophenylarsonic** acids. Data from Table II.

Aromatic sulfone chlorides react with arsanilic and amino-arsanilic acids to give substituted phenylsulfone-aminophenylarsonic acids. These were prepared by the Schotten–Baumann reaction. Of this series, 4-phenylsulfone-aminophenylarsonic acid,[4] 4-p-tolylsulfone-aminophenylarsonic acid,[5] 4-*m*-nitrophenylsulfone-aminophenylarsonic acid[6] and 4-m-nitro-p-tolylsulfone-arninophenylarsonic acid[6] have previously been described.

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[3] Fischer, "Untersuchung über Kohlenhydrate und Ferment," p. 142.

[4] Little, Cohen and Morgan, J. Chem. *Soc.*, 95, 1482 (1909).

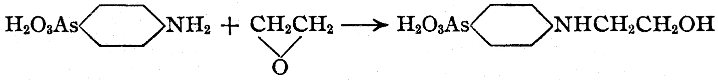
[5] Mouneyrat, French Patent 401,586 (1908); English Patent 142,947 (1919).

[6] Leslie F. Hewitt, H. King **and** W. O. March, J. Chem. *Soc.*, 1355–1370 (1926).

. The present study includes compounds prepared from benzenesulfone chloride and *p*-tolylsulfone chloride with amino-arsanilic acid, and also p-bromobenzene-sulfone chloride with both arsanilic and amino-arsanilic acids. In the case of amino-arsanilic acid only one amino group is involved in the reaction. Judging from the comparative reactivities of the two groups, it is assumed that the amino group in the para position to the arsonic acid is the reactive group.

Highly colored compounds were obtained by condensing picryl chloride with both arsanilic and amino-arsanilic acids in absolute ethyl alcohol, namely, 4-(2,4,6-trinitrophenylamino)-phenylarsonic acid and 4-(2,4,6-trinitrophenylamino)-3-aminophenylarsonic acid.

p-Arsono-anilino-ethanol-2[7] is readily prepared in good yields by the reaction of ethylene oxide and arsanilic acid in the cold.



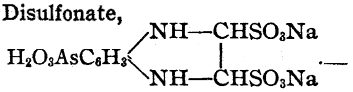
By refluxing arsanilic acid with an excess of o-bromoacetophenone, 4-di-(phenacylamino)-phenylarsonic acid is formed.

$$H_2O_3AsC_6H_4NH_2 + 2BrCH_2COC_6H_5 \longrightarrow H_2O_3AsC_6H_4N(CH_2COC_6H_5)_2 + 2HBr$$

4-Phenacylaminophenylarsonic acid has been prepared by Jacobs and Heidelberger.[8]

Experimental Part

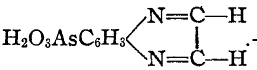
Preparation of 6-Arsonoquinoxaline-2,3-sodium Disulfonate,



$$H_2O_3AsC_6H_3\begin{cases}NH-CHSO_3Na\\ \quad\ \ | \\ NH-CHSO_3Na\end{cases}.—$$

Five grams of amino-arsanilic acid was dissolved in 25 cc. of N sodium hydroxide solution and 6 g. of powdered glyoxal sodium bisulfite added. The reaction mixture was heated to 60° with stirring until the bisulfite compound had dissolved. The solution was filtered and acidified slightly to congo paper with concentrated hydrochloric acid. An equal volume of ethyl alcohol was added to the solution and after standing for a few minutes in the cold a bulky mass of grayish white needles was formed. The product was purified by dissolving in a small amount of water and precipitating with ethyl alcohol as previously described. The yield was 6 g. The product is insoluble in organic solvents but very soluble in water.

Anal. Subs., 0.1583, 0.1615; 0.5631, 0.6250; 0.3861, 0.3144; 14.05, 14.35 cc. of 0.04810 N iodine solution; $BaSO_4$, 0.5686, 0.6470; Na_2SO_4, 0.1202, 0.0984. Calcd. for $C_8H_9O_9N_2S_2Na_2As$: As, 16.22; S, 13.88; Na, 9.95. Found: As, 16.01, 16.02; S, 13.87, 14.22; Na, 10.08, 10.13.

6-Arsonoquinoxaline,  $H_2O_3AsC_6H_3\begin{cases}N=C-H\\ \quad\ \ | \\ N=C-H\end{cases}$.—Five grams of 6-arsonoquinoxaline-2,3-sodium bisulfite was dissolved in 20 cc. of water. After filtering, the solution was heated to boiling and made strongly acid to congo paper with concentrated hydrochloric acid. The solution was boiled with stirring until no mote sulfur dioxide was given off.

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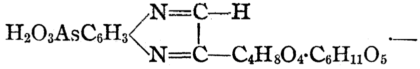
[7] Hamilton, This journal, 45, 2751 (1923).

[8] Jacobs and Heidelberger, *ibid.*, 41, 1590 (1919).

The resulting dark colored precipitate was washed with hot water and purified further by refluxing with water. The green colored product was dried to constant weight by heating at 100" under reduced pressure. The compound is slightly soluble in water and insoluble in organic solvents. It does not melt below 250°.

Anal. Subs., 0.1548, 0.1692; 24.90, 27.35 cc. of 0.04810 N iodine solution. Calcd. for $C_8H_7O_3N_2As$: As, 29.51. Found: As, 29.01, 29.14.

3-Glucosido-erythrityl-quinoxaline-6-arson Acid,

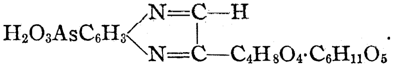


$$H_2O_3AsC_6H_3\begin{cases}N{=}C{-}H\\ \quad\;\; |\\ N{=}C{-}C_4H_8O_4{\cdot}C_6H_{11}O_5\end{cases}.{-}$$

Five grams of maltosone was dissolved in 159 cc. of absolute methyl alcohol and to this was added 3.5 g. of amino-arsanilic acid in 50 cc. of methyl alcohol. The solution was refluxed for three hours and the resulting purple precipitate removed and refluxed with absolute methyl alcohol for purification. The product weighed 4 g. or 60% of the theoretical and did not melt below 250". It is quite soluble in water but is easily hydrolyzed. The red color of its aqueous solution disappears on slight warming and the solution reduces Fehling's solution in the cold, showing the presence of a free osone. The product was heated to constant weight under reduced pressure at 139°.

Anal. Subs., 0.1292, 0.1177; 9.98, 9.00 cc. of 0.04892 N iodine solution. Calcd. for $C_{18}H_{25}O_{12}N_2As$: As, 13.88. Found: As, 14.16, 14.02.

3-Galactosido-erythrityl-quinoxaline-6-arsonc Acid,



$$H_2O_3AsC_6H_3\begin{cases}N{=}C{-}H\\ \quad\;\; |\\ N{=}C{-}C_4H_8O_4{\cdot}C_6H_{11}O_5\end{cases}.$$

One gram of lactosone was dissolved in 25 cc. of hot ethylene glycol and 0.8 g. of amino-arsanilic acid dissolved in 50 cc. of absolute methyl alcohol added. The solution was refluxed for five hours. A light brown substance was precipitated during the heating. The product was filtered from the hot solution and washed with methyl alcohol. The yield was 1.0 g. or 66% of the theoretical. It was purified by working and refluxing with absolure methyl alcohol. The product was dried to constant weight at 100° under reduced pressure.

Anal. Subs., 0.1240, 0 1000; 10.40, 8.40 cc. of 0.04591 *N* iodine solution. Calcd. for $C_{18}H_{25}O_{22}N_2As$: As, 13.88. Found: As, 14.43, 14.45.

Condensation Products of Certain Aldoses with **Arsanilic** Acid.—These reactions were carried out in absolute methyl alcohol. The sugar was dissolved in the least amount of alcohol, filtered and one molecular equivalent of arsanilic acid dissolved in methyl alcohol added. The solution was refluxed from one to four hours, during which time the condensation product was precipitated. They were worked and refluxed with small amounts of methyl alcohol for purification. These compounds are insoluble in organic solvents but quite soluble in water, in which they are readily hydrolyzed. They were dried to constant weight at 45° under reduced pressure.

TABLE I

CONDENSATION PRODUCTS OR ARSANILIC ACID AND ALDOSES

	( )-Aminophenylarsonic acid	Yield, %	Subs.	0 04869 *N* I, cc.	Arsenic, % Calcd.	Arsenic, % Found
1	4-Gluco-, $CH_2OH(CHOH)_4CH{=}NC_6H_4AsO_3H_2$	54	0.1166	12.70	19.83	19.88
2	4-Manno-, $CH_2OH(CHOH)_4CH{=}NC_6H_4AsO_3H_2$	95	.1244	13.65	19.83	20 02
3	4-Galacto-, $CH_2OH(CHOH)_4CH{=}NC_6H_4AsO_3H_2$	90	.1251	13.78	19.83	20.10
4	4-Arabino-, $CH_2OH(CHOH)_3CH{=}NC_6H_4AsO_3H_2$	65	.1018	11.82	21.48	21.19
5	4-Xylo-, $CH_2OH(CHOH)_3CH{=}NC_6H_4AsO_3H_2$	43	.1026	11.82	21.48	21 02

These compounds char below 100°. In obtaining rotation data, 1-2 g. of the substance was dissolved in 25% methyl alcohol in water and made up to 50 cc. with the same solvent. Readings were made in a 2-decimeter tube at a temperature of 22° with sodium light.

TABLE II

OPTICAL ROTATIONS OF 4-ALDO-AMINOPHENYLARSONIC ACIDS

Compounds (Table I)	Subs.	Time of reading (min.) and rotation								
1	1.239	0	15	35	55	75	210	420	640	
		—	−1.30°	−1.14°	−1.05°	−0.98°	−0.70°	−0.20°	+0.10°	
2	1.588	0	12	32	52	72	92	272	472	
		—	−2.50	−2.19	−2.08	−1.96	−1.78	−1.36	−1.19	
3	2.639	0	10	18	24	32	39	50	66	140
		—	−0.67	−0.30	−0.15	+0.25	+0.41	+0.65	+0.78	+0.85
4	1.138	0	10	21	39	55	75	166		
		—	−0.15	+0.35	+0.70	+1.06	+1.25	+1.46		
5	Compound 5 could not be read owing to instant cloudiness of the solution.									

Preparation of Substituted Phenylsulfone-aminophenylarsonic Acids.—The arsonic acids were dissolved in the theoretical amount of N sodium hydroxide and one molecular equivalent of the aromatic sulfone chlorides added. The reaction mixture was heated to boiling with stirring and the mixture refluxed until all of the sulfone chloride had dissolved. The solution was filtered and allowed to cool, the product crystallizing from the cold solution. These compounds were purified by dissolving in *N* sodium hydroxide and precipitating with a slight excess of hydrochloric acid to dissolve any unchanged arsonic acid. The compounds are slightly colored and melt with decomposition. The yields are poor but may be increased by carrying out the reactions in sodium carbonate solution, rather than sodium hydroxide.

TABLE III

SUBSTITUTED PHENYLSULFONE-AMINOPHENYLARSONIC ACIDS

( )-Sulfone-amino-3-aminophenylarsonic acid	Yield, %	M. p., °C. (dec.)	Analysis			
			Subs.	0.05571 *N* I, cc.	Arsenic, % Calcd.	Arsenic, % Pound
4-Phenyl-, $C_6H_5SO_2HN(NH_2)C_6H_3AsO_3H_2$	31	205-7	0.1439	13.80	20.14	20.02
4-*p*-Tolyl-, $CH_3C_6H_4SO_2HN(NH_2)C_6H_3AsO_3H_2$	60	160-5	.1297	12.05	19.41	19.40
4-*p*-Bromophenyl-, $BrC_6H_4SO_2HN(NH_2)C_6H_3AsO_3H_2$	18	180-5	.1244	9.75	16.62	16.33
(4-*p*-Bromophenylsulfone-aminophenylarsonic acid) $BrC_6H_4SO_2HNC_6H_4AsO_3H_2$	33	210-12	.1470	11.82	17.19	16.80

Preparation of 4-(2,4,6-Trinitrophenylamino)-phenylarsonic Acid, $H_2O_3AsC_6H_4NHC_6H_2(NO_2)_3$.—Two grams of arsanilic acid was dissolved in 80 cc. of absolute ethyl alcohol and 3 g. of picryl chloride added. The solution was refluxed for three hours, filtered and cooled to room temperature. Beautiful yellow crystals formed on the sides of the container. The yield was 2 g. or 50% of the theoretical. The substance does not melt below 260°. The product was recrystallized from ethyl alcohol until it gave no test for chlorine.

Anal. Subs., 0.1303, 0.1364; 10.75, 11.35 cc. of 0.05571 *N* iodine solution. Calcd. for $C_{12}H_9O_9N_4As$: As, 17.59. Found: As, 17.22, 17.41.

4-(2,4,6-Trinitrophenylamino)-3-aminophenylarsonic Acid, $H_2O_3AsC_6H_3(NH_2)NHC_6H_2(NO_2)_3$.—This compound was prepared from picryl chloride and amino-arsanilic acid according to the preceding method. It is a deep red colored product and chars at 165°.

Anal. Subs., 0.1040, 0.1261; 8.32, 10.02 cc. of 0.05571 *N* iodine solution. Calcd. for $C_{12}H_{10}O_9N_5As$: As, 16.91. Found: As, 16.70, 16.58.

p-Arsono-anilino-ethanol-2, $H_2O_3AsC_6H_4NHCH_2CH_2OH$.—Forty grams of arsanilic acid was dissolved in 174 cc. of N sodium hydroxide solution and 10 g. of ethylene oxide added. The solution was allowed to stand in a closed container for twenty-four hours at room temperature. The solution was filtered and acidified to congo paper, the white product precipitating immediately. The yield was 24 g. or 50% of the theoretical and the substance melted at 168°. The product was purified by dissolving in N sodium hydroxide solution and precipitating with an excess of concentrated hydrochloric acid.

Anal. Subs., 0.1081, 0.1097; 15.20, 15.30 cc. of 0.05493 N iodine solution. Calcd. for $C_8H_{12}O_4NAs$: As, 28.72. Found: As, 28.95, 28.72.

4-Di-(phenacylamino)-phenylarsonic Acid, $H_2O_3AsC_6H_4N(CH_2COC_6H_5)_2$.—Three grams of arsanilic acid was dissolved in the calculated amount of N sodium hydroxide solution and refluxed with 6 g. of brorno-acetophenone. A yellow colored mass separated after heating the solution for about fifteen minutes; a sufficient amount of N sodium hydroxide solution was added to dissolve the reaction product and the heating continued for ten minutes. The solution was filtered and the excess of bromo-acetophenone extracted by washing with small amounts of ether. The product was precipitated by adding an excess of concentrated hydrochloric acid. The yield was 1.5 g. and the substance melted at 162.5°.

Anal. Subs., 0.1229, 0.1674; 10.90, 14.65 cc. of 0.05240 N iodine solution. Calcd. for $C_{22}H_{20}O_5NAs$: As, 16.73. Found: As, 17.42, 17.20.

Summary

1. Maltosone and lactosone were condensed with amino-arsanilic acid to produce certain new types of arsenated quinoxalines. These compounds are very soluble in water but hydrolyze rapidly.

2. Aldoses condense readily with arsanilic acid to form Schiff bases containing an aromatic arsonic acid and a carbohydrate residue.

3. Further condensation products of arsanilic and amino-arsanilic acids with substituted sulfone chlorides, etc., are given.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

LOCAL ANESTHETICS IN THE PYRROLE SERIES. I[1,2]

BY F. F. BLICKE AND E. S. BLAKE

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The pyrrole or modified pyrrole nucleus is found in a number of naturally occurring compounds—hemoglobin, chlorophyll, proteins, bile and urinary pigments and certain alkaloids. Because of the presence of this nucleus in so many normal physiological products, we decided to introduce it into certain synthetic drugs by the substitution of this group for other cyclic radicals such as phenyl.[3]

Investigations in the chemistry of pyrrole compounds have been retarded by the high cost of pyrrole in this country and by the fact that practical laboratory methods have not been developed for the preparation of relatively large amounts of the simpler pyrrole derivatives.

Recently[4] it was found possible in this Laboratory to prepare pyrrole in fairly large quantities at moderate expense. We began, then, a detailed study of the preparation of pyrrole-carboxylic acids from pyrrole itself[6] and during the investigation of pyrrole-2-carboxylic acid the discovery was made that the ethyl ester of this substance possesses decided local anesthetic action when placed on the tip of the tongue. Although local anesthetic action is a property common to many esters of aromatic acids, especially those of aminobenzoic acids, this type of action, with one exception, has not been noticed hitherto in the case of the esters of the

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[1] This paper represents the first part of a dissertation to be submitted to the Graduate School by Mr. Blake in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] We wish to take this opportunity to acknowledge our indebtedness to Frederick Steams and Company who have made this investigation possible by the grant of a fellowship.

[3] In a few instances comparisons have been made between pyrrole, thiophene and furan compounds and the corresponding benzene derivatives. Because of the close chemical relationship between thiophene and benzene it is not surprising that a number of thiophene derivatives resemble their benzene analogs in taste and odor (Cohn, "Die organischen Geschmacksstoffe," Siemenroth, Berlin, 1914, p. 78). Steinkopf and Ohse have prepared several synthetic drugs in which the thienyl group has been used in place of phenyl. Thiophene-cocaine hydrochloride [*Ann.*, 437, 14 (1924)] and the thiophene analogs of eucaine-A and stovaine [*ibid.*, 448, 205 (1926)] all proved to be strong anesthetics. Diethylamino-ethyl-2-thiophene-carboxylate and diethylamino-ethyl-2-furan-carboxylate [Gilman and Pickens, THIS JOURNAL, 47, 252 (1925)] were found to be poor local anesthetics compared to procaine.

[4] Blicke and Powers, *Ind. Eng. Chem.*, **19**, 1334 (1927).

[5] A number of substituted pyrrole-carboxylic acids have been prepared from aliphatic compounds by ring closure. However, in many instances the yields obtained by this process are poor; furthermore, the method is applicable only for the preparation of certain definite types of pyrrole derivatives.

simpler pyrrole-carboxylic acids. Gilman and Pickens[6] prepared the diethylamino-ethyl ester of pyrrole-2-carboxylic acid and according to Kamm[7] this substance is about one-third as active as procaine.

In addition to the ethyl ester[8] of pyrrole-2-carboxylic acid, we investigated the action of the methyl,[8, 9] propyl,[10] *iso*propyl,[10] butyl,[10] *iso*butyl[10] and *iso*-amyl[10] homologs. It seemed from the rough test on the tip of the tongue that the propyl ester possessed the most decided action. The phenyl ester also possessed some activity. Preliminary pharmacological tests[11] indicate that the ethyl ester is a compound of comparatively low toxicity.

The ethyl esters of pyrrole-1-carboxylic acid, 2-methylpyrrole-3-carboxylic acid[12] and of 2,4-dimethylpyrrole-3-carboxylic acid[13] possessed marked action, but the ethyl esters of the following acids were inactive: 2,5-dimethylpyrrole-3-carboxylic acid,[14] 2,5-diphenyl-pyrrole-3-carboxylic acid,[15] 1,2,5-triphenylpyrrole-3-carboxylic acid,[15] 1,5-diphenyl-2-methylpyrrole-3-carboxylic acid,[16] 1-phenyl-2,5-dimethylpyrrole-3-carboxylic acid,[17] 3-phenyl-5-methylpyrrole-4-carboxylic acid,[13] 2,4-dimethylpyrrole-3,5-dicarboxylic acid,[18] 2,5-dimethylpyrrole-3,4-dicarboxylic acid,[19] 2-pyrrolidone-5-carboxylic acid[20] and 3,4,5-tribromopyrrole-2-carboxylic acid.

Mannich and co-workers[21] found, unexpectedly, that β-N-piperidinoethyl phenyl ketone, $C_6H_5COCH_2CH_2NC_5H_{10}$, a substance obtained readily from acetophenone, piperidine hydrochloride and paraformaldehyde, possesses local anesthetic action. Furthermore, the benzoyl derivative of the corresponding secondary carbinol, $C_6H_5CH(OCOC_6H_5)CH_2CH_2NC_5H_{10}$, was shown to be a strong anesthetic. We prepared the above ketone by another process, a method which indicates definitely the structure of the substance, namely, by the action of β-bromopropiophenone on piperidine

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[6] Giman and Pickens, THIS JOURNAL, 47, 245 (1925).

[7] Kamm, *ibid.*, 47, 252 (1925).

[8] (a) Ciamician and Silber, Ber., 17, 1152 (1884); (b) Oddo, *Gazz. chim.* ital., I, 39, 658 (1909).

[9] Oddo and Moschini, Gazz. *chim.* ital., II, 42, 252 (1912).

[10] This ester has been prepared from pyrrylmagnesium bromide and the alkyl chloroformic ester by Oddo and Moschini, Gazz. *chim.* ital., II, 42, 253 (1912).

[11] Conducted in the Laboratories of Frederick Stearns and Company.

[12] Benary, Ber., 44, 495 (1911).

[13] Knorr and Lange, ibid., 35, 3007 (1902).

[14] Hantzsch, *ibid.*, 23, 1475 (1890).

[15] Kapf and Paal, ibid., 21, 3060 (1888).

[16] Lederer and Paal, ibid., 18, 2595 (1885).

[17] Feist, ibid., 35, 1546 (1902).

[18] Knorr, *Ann.*, 236, 318 (1886).

[19] Knorr, Ber., 18, 302 (1885).

[20] Haitinger, Monatsh., 3, 228 (1882); Abderhalden and Kautzsch, Z. *physiol.* Chem., 78, 115 (1912).

[21] Mannich and Lammering, *Ber.*, 55, 3515 (1922); German Patent, 379,950; *Friedländer*, 14, 1247; Mannich and Curtas, Arch. *Pharm.*, 264, 750 (1926).

$$C_6H_5COCH_2CH_2Br + 2HNC_5H_{10} \longrightarrow C_6H_5COCH_2CH_2NC_5H_{10} + HNC_5H_{10}\cdot HBr$$

From bromo-acetophenone and piperidine we obtained N-piperidinomethyl phenyl ketone, $C_6H_5COCH_2NC_5H_{10}$, the lower homolog of the above ketone. This latter compound, as well as the benzoate of the corresponding secondary alcohol, $C_6H_5CH(OCOC_6H_5)CH_2NC_5H_{10}$, was found to possess anesthetic activity.

2-Acetylpyrrole, piperidine hydrochloride and paraformaldehyde react readily to form a substance which possesses marked anesthetic action. Based on analogy the compound should have the structure $C_4H_4NCOCH_2CH_2NC_5H_{10}$. Unfortunately, we were unable to obtain this material in crystalline condition.

Experimental Part

Pyrrole.—We wish to add the following notes to the information published previously[4] concerning the preparation of pyrrole.

For the preparation of ammonium mucate on a large scale about three and one-half times the amount of ammonia water (technical) required theoretically was added to mucic acid which had been put into a large crock. The mixture was stirred thoroughly from time to time. After several weeks, through evaporation of the water, the ammonium salt was obtained in the form of a thick paste. The latter was transferred to galvanized iron trays and allowed to dry thoroughly. The material was then milled to a flour-like powder.

It was found advantageous to replace the metal coil condenser by two ordinary glass bulb condensers.

As soon as the mixture of pyrrole, water and ammonium carbonate begins to distil from the apparatus at a fairly rapid rate, the Fletcher burner should be replaced by a micro burner. If the bottom of the apparatus is heated too strongly at this stage of the operation the reaction mixture invariably foams over into the condenser.

After 200–250 cc. of pyrrole (this refers to experiments in which 5.5 pounds of ammonium mucate have been used) has been collected, the formation of pyrrole becomes so slow that it seems that the process is complete. The micro burner should now be replaced by a Fletcher burner. The distillation of pyrrole then begins again and at least 100 cc. more of pyrrole is obtained.

The crude pyrrole contains considerable ammonia and this should be removed by treatment of the material with a small amount of water.

Contrary to the statements in the literature,[22] we found that pyrrole is appreciably soluble in water and in a saturated solution of ammonium carbonate. One hundred cc. of water dissolves about 5 cc. of pyrrole at ordinary temperature. The aqueous ammonium carbonate layer obtained in the preparation of pyrrole should be extracted with ether.

To obtain pyrrole in a colorless state it should be distilled in a stream of dry nitrogen and kept in sealed ampules, under nitrogen, protected from light.

Ethyl Ester of Pyrrole-1-carboxylic Acid.[23]—This compound was prepared from

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[22] Schwanert, *Ann.*, **116**, 279 (1860); Beilstein, "Handbuch der organischen Chemie," 1899, vol. IV, p. 64.

[23] Ciamician and Dennstedt, *Ber.*, **15**, 2579 (1882); *Ann.*, **210**, 400 (1881); Tschelinseff and Maxoroff, *J. Russ. Phys.-Chem. Soc.*, **1**, 161 (1915); Tschelinseff and Maxoroff, *Ber.*, **60**, 196 (1927). The latter investigators (*ibid.*, p. 195) were able to isolate the unstable pyrrole-1-carboxylic acid and studied a number of its derivatives.

potassium pyrrole and ethyl chloroformate. The potassium pyrrole can be prepared rapidly by the use of excess pyrrole as a solvent as described in a later experiment. The potassium compound, which precipitates when the hot concentrated solution is cooled, is filtered and washed with absolute ether.

In an attempt to rearrange the ester into the ethyl ester of pyrrole-2-carboxylic acid, the material was passed through a hot combustion tube. The only products which we were able to identify were ethylene and a very small amount of pyrocoll. The ethylene was isolated as ethylene bromide; b. p. 128".

Esters of Pyrrole-2-carboxylic Acid.—Pyrrole-2-carboxylic acid was obtained from pyrrylmagnesium bromide and carbon dioxide.[24] The dark colored acid was purified in the following manner. The substance was dissolved in somewhat more than the required amount of ammonium hydroxide. The solution was diluted and then boiled for a short time with "nuchar." The mixture was filtered and the filtrate cooled with ice. After the addition of ether the colorless solution was stirred and dilute sulfuric acid added in small amounts. The carboxylic acid was obtained from the ether solution in a practically colorless state. It was found that in some instances the acid did not dissolve readily in ether if it had been precipitated completely and then treated with a solvent.

In order to prepare the alkyl esters an excess of the alkyl halide was heated in a pressure bottle, immersed in a bath of boiling water, with the silver salt of pyrrole-2-carboxylic acid; in some instances, however, we refluxed a mixture of the alkyl bromide, the silver salt of the acid and toluene. The crude esters boiled over a considerable range of temperature and the distillate was collected in several portions. The fractions used in our tests boiled as follows: methyl ester, 220–223° (m. p. 72–73'); ethyl ester, 227–230° (m. p. 38–40°); n-butyl ester, 255–260° (m. p. 36–38°); *iso*butyl ester, 250–255° (m. p. 68-69"); iso-amyl ester, 263–267°. The barometric pressure was 740 mm.

According to Ciamician and Silber[8a] bromination of the methyl ester of pyrrole-2-carboxylic acid yields a tribromo derivative. We brominated the ethyl ester in the presence of water according to the method described by the above-mentioned investigators. A tribromo substitution product was formed which, after recrystallization from acetic acid and then from alcohol, melted at 195–196°. Anal. Calcd. for $C_7H_6O_2NBr$: Br, 63.79. Found: Br, 63.75. The following preparative method was found to be much more satisfactory. To 1.4 g. of the ester, dissolved in 5 cc. of acetic acid, there was added slowly, with cooling, 1.6 cc. (3 molecular equivalents) of bromine dissolved in 5 cc. of acetic acid. The bromine was decolorized almost instantly with the evolution of hydrogen bromide and the greater part of the bromo ester separated from the solution. The product was recrystallized twice from acetic acid and then from alcohol; m. p. 195–196°. The compound dissolves in warm, aqueous sodium hydroxide. Upon acidification of the solution a gelatinous precipitate was obtained. The latter melted at 195° after recrystallization from acetic acid. In view of the fact that the compound can be recovered unchanged from an alkaline solution and that the methyl ester of tribromopyrrole-2-carboxylic acid yields a tribromopyrrole-2-carboxylic acid upon hydrolysis,"' it seems certain that the bromine atoms in the bromo esters occupy the nuclear positions 3, 4 and 5.

The phenyl ester was obtained in the following manner. The acid chloride obtained from 3 g. of pyrrole-2-carboxylic acid was dissolved in ether and heated for two hours on a steam-bath with sodium phenolate which had been prepared from 2.5 g. of phenol, 0.62 g. of sodium and 70 cc. of absolute ether. The mixture was treated

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[24] Oddo, *Gazz.* chim. ital., I, 39, 649 (1909); I, **44**, 482 (1914); *Ber.*, **43**, 1012 (1910); McCay and Schmidt, THIS JOURNAL, **48**, 1935 (1926).

with dilute sodium hydroxide, then with water, and the ether layer dried over fused sodium sulfate. After removal of the ether a dark colored, oily residue was obtained. The material was dissolved in hot petroleum ether (30–60°). When the solution was cooled crystals were obtained which melted at 44–45°. The yield was **2.8** g.

Anal. Subs., **0.2350;** CO_2, **0.6089;** H_2O, **0.1035.** Calcd. for $C_{11}H_9O_2N$: C, **70.56;** H, **4.85.** Found: C, **70.66;** H, **4.93.**

β-*n*-Piperidino-ethyl Phenyl **Ketone.**—β-Bromopropionic acid was mixed with three times the calculated amount of thionyl chloride. After two days the excess thionyl chloride was removed under diminished pressure. The acid chloride of β-bromopropionic acid was then distilled; b. p. **69–71"** under **23** mm. pressure.[25]

Thirty grams of the acid chloride **(0.17** mole) was dissolved in **150** cc. of dry benzene and **28** g. of aluminum chloride **(0.21** mole) was added in small portions.[26] After twenty-four hours the reaction mixture was decomposed with ice and hydrochloric acid. Upon removal of the excess benzene under diminished pressure the residue became crystalline. The β-bromopropiophenone melted at **59–60**° after recrystallization from alcohol. The yield was **29** g. or 80% of the calculated amount. The halogen is removed rapidly from the bromo ketone when the latter is heated with alcoholic sodium hydroxide.

Anal. Calcd. for C_9H_9OBr: Br, **37.51.** Found: Br, **37.62.**

Ten cc. of piperidine **(0.1** mole) dissolved in **50** cc. of absolute ether was added slowly to **10.6** g. **(0.05** mole) of β-bromopropiophenone, dissolved in **70** cc. of the same solvent. Eight and one-tenth grams of piperidine hydrobromide precipitated immediately. The calculated amount of piperidine hydrobromide is **8.2** g. After removal of the piperidine salt the ether layer was washed with water and then dried thoroughly with fused sodium sulfate. The solution was filtered and then treated with dry hydrogen chloride. There precipitated **8.3** g. of the hydrochloride of β-*n*-piperidino-ethyl phenyl ketone. The calculated yield of the hydrochloride is **12.6** g. The salt melted at 187–188°.[27] The melting point was unchanged after recrystallization from ethyl acetate to which a few drops of alcohol had been added. We prepared the ketone hydrochloride by the method of Mannich and Lammering;[27] the material melted at **182–183°.**

The ketone was reduced to the secondary carbinol in the following manner. The hydrochloride described above was dissolved in water and the free base liberated by the addition of sodium hydroxide. Five g. of the oily base, dissolved in **50** cc. of absolute alcohol, was reduced with hydrogen in the presence of **0.35** g. of platinum oxide catalyst[28] under an initial pressure of four atmospheres. The calculated amount of hydrogen was absorbed in about twenty minutes. The carbinol was obtained in solid form after removal of the alcohol; m. p. **64–65"** after recrystallization from petroleum ether (30–60°).[29] The hydrochloride precipitated immediately when hydrogen chlo-

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[25] The acid chloride would probably distil without decomposition under ordinary pressure.

[26] Collet, Bull. *soc. chim.*, **[3] 17, 66** (1897), studied the interaction of a number of halogenated acid chlorides and benzene in the presence of aluminum chloride. He found that only the acyl halogen reacts readily with the benzene.

[27] Mannich and Lammering, *Ber.*, **55, 3515** (1922), recorded the melting point as 192–193° and stated that the hydrochloride can be recrystallized from a mixture of dilute alcohol and acetone.

[28] "Organic Syntheses," John Wiley and Sons, Inc., New York, **1928,** Vol. VIII, p. **92.**

[29] Mannich and Lammering, *Ber.*, **55, 3517** (1922), state the melting point to be 68–69°. They reduced the amino-ketone hydrochloride with hydrogen in the presence of palladium-charcoal.

ride was passed into an ether solution of the carbinol; m. p. 139–140°. Upon benzoylation of the carbinol in chloroform the benzoate described by Mannich and Lammering was obtained. Hydrolysis of the benzoate with alcoholic sodium hydroxide yielded the secondary carbinol which melted at 64–65° after recrystallization from petroleum ether.

n-Pipefidinomethyl Phenyl Ketone.—To 16 g. of bromo-acetophenone[30] dissolved in 100 cc. of absolute ether there was added 16 cc. of piperidine dissolved in 50 cc. of the same solvent. The calculated amount of piperidine hydrobromide precipitated at once. The piperidino ketone was obtained in the form of an oil which exhibited marked local anesthetic action on the tongue. The hydrochloride was obtained in crystalline form from an ether solution of the ketone and hydrogen chloride. It can be recrystallized from ethyl acetate to which a few drops of alcohol have been added; m. p. 210–211°. The hydrochloride possesses anesthetic action.

In order to prepare the secondary carbinol 10.5 g. of the ketone was dissolved in 50 cc. of absolute alcohol and reduced with hydrogen in the presence of 0.5 g. of platinum oxide catalyst. The initial pressure was four atmospheres. After thirty minutes the reduction seemed to be complete. A solid material was obtained which, after recrystallization from petroleum ether, melted at 69–70'. The hydrochloride melts at 193–194°.

Anal. Subs., 0.2201: CO_2, 0.6143; H_2O, 0.1854. Calcd. for $C_{13}H_{19}OH$: C, 76.02; H, 9.33. Found: C, 76.11; H, 9.42.

The secondary carbinol was benzoylated in the following manner. One gram of the carbinol was dissolved in 25 cc. of absolute ether. The required amount of benzoyl chloride, dissolved in ether, was added. Seven-tenths of a gram of the hydrochloride of the benzoate precipitated; m. p. 193–194°. The free base was obtained in the form of an oil. The hydrochloride and the free base both possess anesthetic action. The melting point of the carbinol, obtained by hydrolysis of the benzoate, was 69–70°.

n-Piperidinomethyl 2-Pyrryl Ketone.—Twelve and one-tenth grams of piperidine hydrochloride, 30 cc. of absolute alcohol and 4.5 g. of paraformaldehyde were heated and 10.9 g. of 2-acetylpyrrole was added during the course of half an hour. An additional 3 g. of paraformaldehyde was then added and the mixture heated for fifteen minutes longer. After evaporation of the alcohol the ketone was obtained in the form of an oily hydrochloride. The latter was dissolved in water and the free base precipitated by the addition of sodium hydroxide. The oily base possessed anesthetic action.

Summary

It has been found that a number of esters of pyrrole-carboxylic acids, especially the alkyl esters of pyrrole-2-carboxylic acid, possess marked local anesthetic action on the tongue.

n-Piperidinomethyl phenyl ketone, n-piperidinomethyl 2-pyrryl ketone and the benzoate of *n*-piperidinomethylphenylcarbinol were found to possess local anesthetic action.

ANN ARBOR, MICHIGAN

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[30] Mohlau, *Ber.*, 15,2465 (1882).

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORIES OF THE UNIVERSITY OF UPSALA AND THE NEW YORK AGRICULTURAL EXPERIMENT STATION]

THE MOLECULAR WEIGHT OF CASEIN. I[1]

BY T. SVEDBERG, L. M. CARPENTER AND D. C. CARPENTER[2]

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The molecular weight of casein was first estimated by Van Slyke and Bosworth[3] from the sulfur and phosphorus content. These workers found 0.72% of sulfur and 0.71% of phosphorus in a sample of casein, and assuming one atom of each of these elements in the original protein arrived at the value 4444. For no clear reason they doubled this value and set down the probable molecular weight as *8888.* As to their method of preparing casein, which involves heating for some time in alkaline solution, Harden and Macallum[4] have called attention to the fact that no doubt hydrolytic cleavage of part of the sulfur and phosphorus of the protein has taken place during the preparation. Experiments by one of the writers,[5] while not bearing directly on the matter of sulfur and phosphorus cleavage, show that there is considerable cleavage of nitrogen of the casein molecule under the conditions which Van Slyke and Bosworth imposed on their material. This substantiates the claims of Harden and Macallum and shows that Van Slyke and Bosworth's material and calculations based thereon cannot be seriously considered.

Pauli and Matula[6] ingeniously attempted to evaluate the valency of casein through application of the Ostwald dilution rule. Using this rule they concluded that the valency of casein was 3. Since they found the combining weight of casein for base was about 1000, they concluded that the molecular weight was 3000.

Yamakami[7] examined the molecular weight of casein by Barger's method, which compares solutions of equal vapor pressure. He concluded that for the simplest alkali caseinates which he could prepare, the mean weight of the ions was about 2000, which would mean for a caseinate dissociating into only two ions a molecular weight of about 4000. This figure would then necessarily represent only a minimum value for the molecular weight.

More recently Cohn, Hendry and Prentiss[8] have attempted to evaluate

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[1] Read before the Meeting of the American Chemical Society at Columbus, Ohio, on May 2,1929.

[2] Fellow of the International Education Board.

[3] Van Slyke and Bosworth, J. *Biol. Chem.*, 14,203,228 (1913).

[4] Harden and Macallum, *Biochem.* J.,8, 90 (1914).

[5] D. C. Carpenter, J. *Biol. Chem., 67,647* (1926).

[6] Pauli and Matula, *Biochem. Z.,* 99,219 (1919).

[7] Yamakami, *Biochem. J.,* 14,522 (1920).

[8] Cohn, Hendry and Prentiss, *J. Biol. Chem.*, 63,721 (1925).

the molecular weight of several proteins from their amino acid content. With considerable reluctance they placed the molecular weight of casein at 192,000. On the basis of one molecule of cystine per molecule of casein, the minimal molecular weight of casein was calculated to be 96,000. However, largely on account of the difficulty of fitting the tryptophan content to this latter value, they decided in favor of the value 192,000.

Researches on casein in late years have usually started with preparations made either by the method of Hammarsten[9] or by the method of Van Slyke and Baker.[10] We have examined casein made by each of these methods, by means of the ultracentrifuge, and in this paper will report experiments based on Hammarsten casein.

The recent experiments of Kondo,[11] Linderstrorn-Lang and Kodama,[12] and Linderström-Lang[13] seem to show that Hammarsten casein is a mixture of substances, inasmuch as they found the solubility in dilute hydrochloric acid to be dependent on the casein content of the solution.

Gortner[14] criticized these workers on the ground that they had not removed an alcohol-soluble protein from their material, which had previously been separated and identified by Osborne and Wakeman.[15] Although Gortner may have been right in part, Osborne and Wakeman reported a yield of their alcohol-soluble protein entirely too low to account for the results obtained by the workers in the Carlsberg laboratory.

In view of the discordant state of the literature relating to casein, it was considered advisable to undertake an investigation of this important protein by means of the centrifugal methods developed in this Laboratory[16] and already used for the determination of the molecular weights of hemoglobin,[17] egg albumin,[18] phycocyan, phycoerythrin,[19] hemocyanin,[20] serum albumin and serum globulin[21] and edestin.[22]

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[9] Hammarsten, "Handbuch der biochemischen Arbeitsmethoden," E. Abderhalden, Berlin und Wien, 1910, Vol. II, p. 384.

[10] Van Slyke and Baker, *J. Biol. Chem.*, 35, 127 (1918).

[11] Kondo, *Compt. rend. trav. lab. Carlsberg*, 15, No. 8 (1925).

[12] Linderström-Lang and Kodama, *ibid.*, 16, No. *1* (1925).

[13] Linderström-Lang, *Z. physiol. Chem.*, 176, 76 (1928); "Dissertation," Copenhagen, 1929.

[14] Gortner, "Casein and Its Industrial Applications," Sutermeister, New York, 1927, p. 14.

[15] Osborne and Wakeman, *J. Biol. Chem.*, 33,243 (1917).

[16] Svedberg, *Z. physik. Chem.*, **121**, 65 (1926); *ibid.*, 127, 51 (1927).

[17] Svedberg and Fåhraeus, THIS JOURNAL, 48, 430 (1926); Svedberg and Nichols, *ibid.*, 49, 2920 (1927).

[18] Svedberg and Nichols, *ibid.*, 48,3081 (1926).

[19] Svedberg and Lewis, *ibid.*, 50, 525 (1928).

[20] Svedberg and Chirnoaga, *ibid.*, 50, 1399 (1928); Svedberg and Heyroth, *ibid.*, 51, 539, 550 (1929).

[21] Svedberg and Sjögren, *ibid.*, 50, 3318 (1928).

[22] Svedberg and Stamm, *ibid.*, 51,2170 (1929).

Experimental

The casein used in this investigation has in every instance been prepared from cow's milk and in so far as possible was obtained from the same dairy herd. As casein is practically insoluble at its isoelectric point, PH 4.7, we have carried out our centrifuging experiments in phosphate buffer solutions of *PH* 6.8, this *PH* value closely approximating that of freshly drawn milk.

Preparation of Material.—Milk was drawn from the animal into flasks containing toluene, brought to the laboratory at once and cooled to 5° as rapidly as possible. Butter fat was removed from the cold milk by slow passage through a milk separator operated at *13,200* r.p m. In this operation practically all the fat was removed from the milk and clung firmly to the center shaft and disks of the separator. Some "separator slime" collected on the sides of the bowl and was discarded.

The separated milk was diluted with 4 volumes of cold water and the casein precipitated by the Hammarsten method[9] through the slow addition of diluted (1:100) acetic acid, the diluted milk being mechanically stirred meanwhile. This operation required the equivalent of 7.5 cc. of glacial acetic acid per liter of milk. The precipitated casein settled rapidly and after washing by decantation several times with water, the precipitate was centrifuged from the wash water and several additional washings made, separating the casein each time centrifugally.

The moist precipitate was then dissolved in dilute ammonia, adding the ammonia slowly during mechanical agitation so as to have no pronounced alkalinity at any time in any part of the solution. (The PH of the solution was kept below 7.0.) The ammonium caseinate solution was then passed slowly through the separator and after diluting with water the casein was precipitated by the calculated amount of dilute acetic acid as before. The precipitate was washed with water, redissolved in ammonia and again reprecipitated with dilute acetic acid and washed repeatedly. Hammarsten[23] showed that further reprecipitation does not improve the purity of the product.

A portion of the moist casein (2 g., dry basis) was then dissolved in *25* cc. of $M/15$ mixed phosphate buffer solution (PH *6.8)* in the cold and diluted to 100 cc., thereby making the buffer salt concentration $M/60$. The solution was stored at 5° with toluene as preservative. This is hereinafter referred to as Hamrnarsten casein.

Another portion of the moist casein *(13* g., dry basis) was extracted at 40° for one hour with two liters of 70% ethyl alcohol containing 1 cc. of normal hydrochloric acid per liter, after the manner of Linderström-Lang.[12,13] The solution was separated from undissolved casein in a centrifuge. (The extraction was continued with a second two-liter portion of acidified alcohol which was separated again in the centrifuge from undissolved material.) From the first extraction with 2 liters of acidified alcohol. 2.15 g. of material (dry basis) was reclaimed by precipitation with dilute sodium hydroxide and from the second extraction 2.19 g. was reclaimed in the same manner. These fractions were dissolved separately in 25-cc. portions of $M/15$ mixed phosphate buffer solution (PH *6.8)* in the cold, diluted to 100 cc. and stored at 5° with toluene. This is hereinafter referred to as acid–alcohol soluble casein, and would probably correspond to fractions K_3, K_4 and K_5 of Linderstrom-Lang's nomenclature. The undissolved casein residue from the above treatment was not further extracted or examined.

Specific Volume.—The partial specific volume was determined pycnometrically **at** 19.8". The amount of protein in solution was found by drying a sample of the stock solution to constant weight at 105° and corrected for the amount of residue due to the

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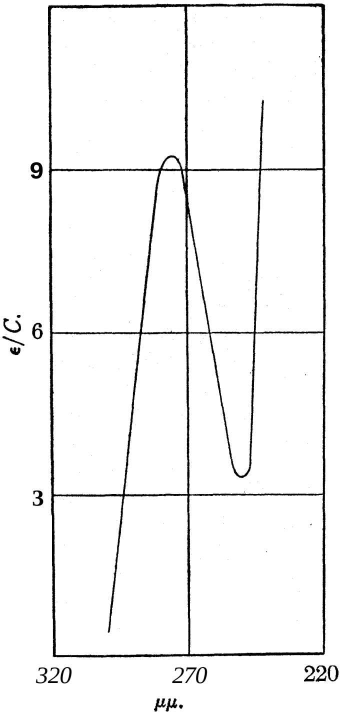
[23] Hammarsten, *Z. physiol.* Chem., 7,227 *(1883).*

buffer salts themselves. This method has been shown to give results identical with those obtained by removing the protein by some precipitation process and weighing directly.

The partial specific volume was found to be 0.750 and was independent of concentration, within the limits of experimental error, for protein concentrations between 1.0 and 2.0%. This value closely approximates similar values for several proteins already examined.

Light Absorption.—Experiments were carried out by means of the Judd–Lewis spectrophotometer to determine the absorption in the short-waved ultraviolet part of the spectrum. The toluene used as preservative in the protein solutions was first removed by bubbling moist nitrogen gas through the solution before measuring the light absorption. The solutions were examined at PH 5.9, 6.8 and 8.0 in 20-mm. cells with protein contents, respectively, of 0.02, 0.05 and 0.10%. The specific extinction coefficient $\epsilon/C = 1/Cd \log I_0/I$, where C is the protein concentration in per cent., I_0 the intensity of the light beam after passing a layer of solvent d cm. in thickness and I the intensity after passing the same thickness of protein solution. The extinction coefficient is plotted against wave length in Fig. 1.



Pig. 1.

The absorption curve has a maximum at 276μμ and a minimum at 250μμ. The values of the extinction coefficient fall somewhat below those reported for serum globulin but are higher than for the other proteins thus far examined in this Laboratory. This order is to be expected if the extinction coefficient in this region is due to the tryptophan content of the protein molecule. Differences in extinction coefficient due to differences in PH of the solutions fell within the experimental error.

Hammarsten Casein.—Several runs were made by the sedimentation velocity method with solutions containing various concentrations of Hammarsten casein. In Tables I and II are recorded data of a representative sedimentation series at an initial protein content of 0.75%. The sedimentation curves for this run are shown in Fig. 2.

The unusual shape of the sedimentation curves (Fig. 2) suggests at once that we are not dealing with a monomolecular substance, but rather with a substance containing several different kinds of molecules. Similar curves have been obtained for other proteins which were in a state of change. To arrive at an approximation, we have assumed that the upper break in the successive curves occurs at about their respective points of intersection with the line AB. On this basis we have calculated the specific sedimentation velocity and the "apparent" diffusion constant as shown in Tables I and II.

TABLE I

HAMMARSTEN CASEIN. SEDIMENTATION VELOCITY RUN

Initial protein concentration, **0.75%;** solvent, $M/60$ mixed phosphate buffer at Pa **6.8;** speed, **43,500** r.p.m. ($\omega = 1450\pi$); interval between exposures, **15** min.; T = **295.2";** illumination, mercury lamp; light filters, Cl_2 and Br_2; Imperial Process photographic plates; exposure time, **70** sec.; metol–hydroquinone developer; development time, **2** min.

Sedimentation curves used[a] in calcn.	ΔX, cm.	X, mean. cm.	$S_{20°}$, cm. X 10^{-13}
3–4	0.064	4.787	6.83
4–5	.062	4.850	6.53
5–6	.058	4.910	6.04
6–7	.053	4.965	5.46
7–8	.060	5.022	6.11
8–9	.057	5.080	5.74
9–10	.056	5.137	5.55
		Mean	5.97

[a] Sedimentation curves bear the same number in Fig. **2** as **in** these data.

TABLE II

HAMMARSTEN CASEIN. DIFFUSION MEASUREMENTS

Initial protein concentration, **0.75%:** same experimental details as given in Table **I**

Reading[a]	Diffusion time, sec.	Mean[b] Z, cm.	"Apparent" $D_{20°}$, cm.^{2}/sec. X 10^{-7}
3	1080	0.027	7.03
4	1980	.041	8.84
5	2880	.052	9.78
6	3780	.0705	13.69
7	4680	.0835	15.51
8	5580	.0950	16.84
9	6480	.1150	21.26
10	7380	.1345	25.53

[a] Reading number refers to corresponding sedimentation curve in Fig. **2.**

[b] "Mean Z" represents the mean of the distances from C = **25%** to **C** = **50%** and from C = **50%** to **C** = 75%, see THIS JOURNAL, **49,2922 (1927).**

It will be noted that the "apparent" diffusion constant is not at all constant and that the value increases as the experiment proceeds. This is evidence that we are dealing with a mixture of substances.

If we assume a spherical particle and apply Stokes' Law

$$r = \sqrt{\frac{9\eta s}{2(\rho_1 - \rho_2)}}$$

in which r is the radius of the particle, η the viscosity of the solvent, s the specific sedimentation velocity and $(\rho_1 - \rho_2)$ the difference in density between particle and solvent, we find that the particle radius is 2.85×10^{-7} cm. From Einstein's equation

$$D = \frac{RT}{N} \times \frac{1}{6\pi r\eta}$$

we calculate that a spherical particle of this radius will have a diffusion constant equal to 7.48×10^{-7}. This will distinctly be a limiting case and one in which the frictional force opposing the motion of the sphere will be a minimum. In other words, the maximum diffusion constant we can possibly expect would be 7.48×10^{-7}. That we find higher values than this shows that the "apparent" diffusion must be due to a spreading out of the boundary on account of the presence of molecules of more than one size.

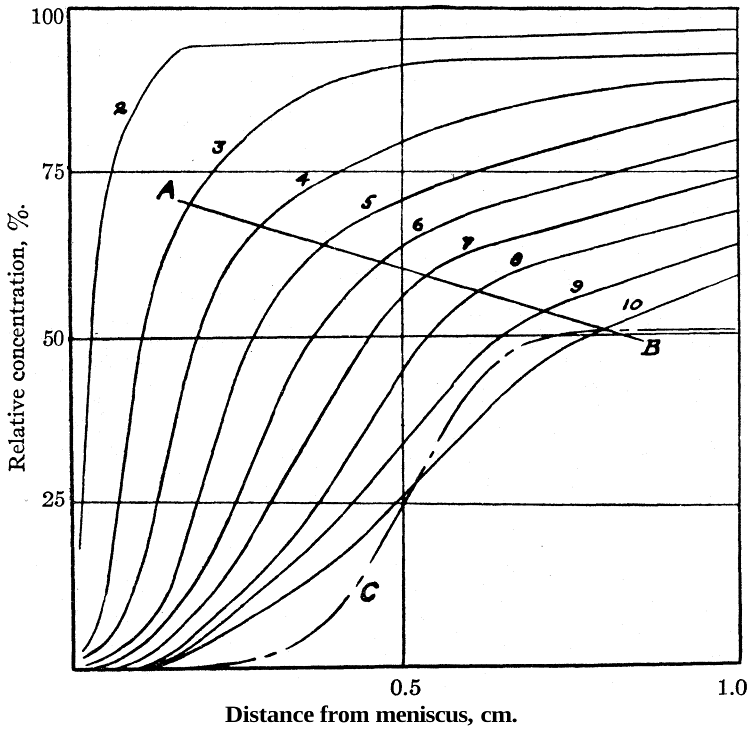


Fig. 2.

The broken line C in Fig. 2 represents how a monomolecular system having $S_{20^\circ} = 5.97 \times 10^{-13}$ and $D_{20^\circ} = 7.48 \times 10^{-7}$ would have been distributed under the same conditions as in Curve 10.

From these experiments we are forced to conclude that Hammarsten casein is a mixture of protein molecules of different weight.

Acid–Alcohol Soluble Casein.—The protein material extracted from Hammarsten casein by warm 70% ethyl alcohol containing 1 cc. of hydrochloric acid per liter[12,13] was examined in the ultracentrifuge by both the sedimentation velocity and the equilibrium methods.

Sedimentation Velocity Method.—Sedimentation velocity runs were made at various protein concentrations between **0.32** and 1.50%. A summary of these runs is given in Table III. A graph showing the relationship between concentration and specific sedimentation velocity is to be found in Fig. 3. It is to be noted that as the protein solution is progressively diluted with $M/60$ phosphate buffer the specific sedimentation velocity is found to increase rapidly until the concentration 0.45% is reached, below which concentration the sedimentation velocity remains practically constant. It is inferred that in concentrations of this protein above 0.45% the protein particles in the solutions are sufficiently close together to have an interfering effect on the free movement of one another and hence the normal diffusion and sedimentation rates are lowered.

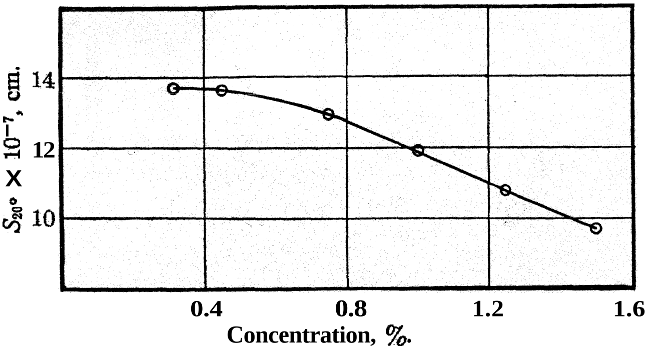


Fig. 3.

TABLE III

ACID–ALCOHOL SOLUBLE CASEIN. SUMMARY OF SPECIFIC SEDIMENTATION VELOCITY VALUES

Concn., %........	1.50	1.25	1.00	0.75	0.45	0.32
	Mean $S_{20°}$ cm. × 10^{-13}					
	8.62[a]	10.14	11.30	12.02[a]	12.40	13.95
	8.90[a]	10.33	11.56	12.95	13.84	13.73
	9.39	10.80	12.00	12.85	13.57	13.70
	9.74	11.05	12.22	12.66	13.06	13.32
	9.76	11.64	12.51	13.10	14.38	13.88
	9.79	12.01[a]	13.60[a]	12.59	14.60	13.68
	9.70				13.62	
Mean $S_{20°}$........	9.68	10.79	11.92	12.83	13.64	13.72

[a] Value discarded in calculating mean.

As we are primarily interested in the more dilute solutions, for this reason we will direct attention to those solutions in which the protein concentration is sufficiently low to eliminate inter-particle forces tending to disturb the free motion of the individual particle.

In Fig. 4 is shown the photographic record of a sedimentation run at 43,600 r.p.m. on a solution containing 0.45% of protein. The progress of sedimentation as the experiment proceeds is shown in the upper row of photographs, while the lower row represents the concentration scale from pure buffer solution (left side) by successive increases to the initial concentration of the protein solution centrifuged (right side). In Fig. 5 are shown the sedimentation curves representing the distribution in a series of photographs obtained in a duplicate run to Fig. 4, at a speed of about 25,000 r.p.m.

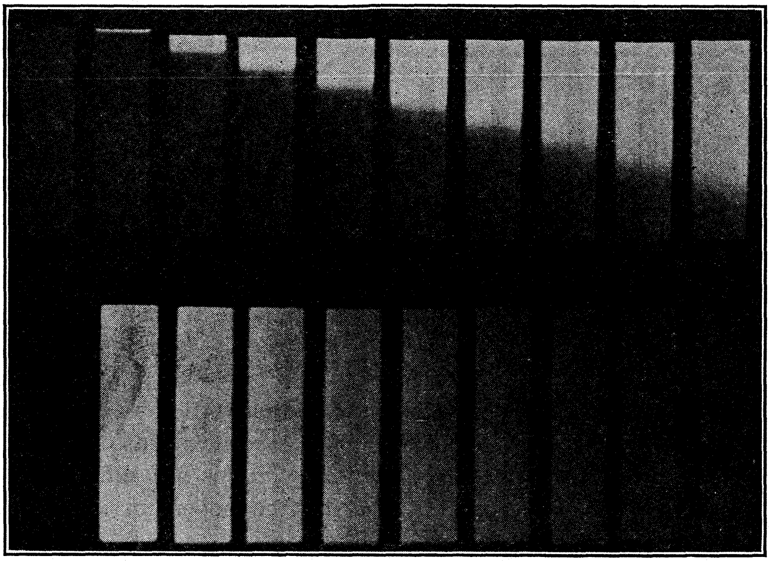


Fig. 4.

The diffusion constant for this protein was found to be 3.56 X 10^{-7} at concentrations below 0.45%. This value represents a mean of several well-agreeing determinations. In Fig. 5 the circles represent the theoretical distribution after three hours at the boundary of a monomolecular substance having a diffusion constant of 3.56 X 10^{-7}. The excellent agreement between theory and experiment is all that can be asked of the experimental method.

In Table IV are recorded the sedimentation data on the above run, showing that the mean specific sedimentation velocity at 20° equals 13.64 X 10^{-13} when the concentration is 0.45% protein. Another run at 0.32% protein concentration gives $S_{20^\circ} = 13.72 \times 10^{-13}$.

Using the above data for S_{20° and D_{20° we have calculated the molecular weight of this protein from the equation $M = RTS/D(1 - V_\rho)$ where M = molecular weight, S = specific sedimentation velocity, V = partial specific volume of the protein, ρ = density of solvent, and R, T and D have the usual significance. In the solutions of 0.32% and 0.45% the molecular weight was found to be 375,000 and 373,420, respectively, the former number being perhaps preferable to the latter.

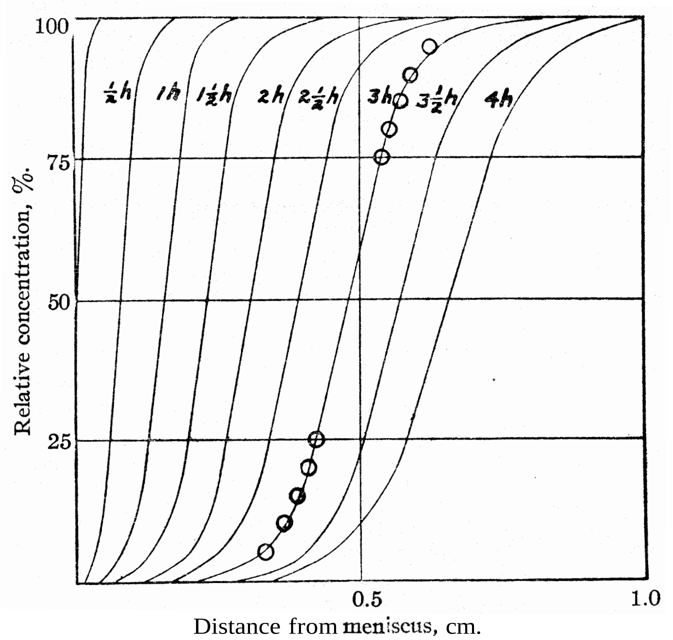
Table IV

Acid–Alcohol Soluble Casein. Specific Sedimentation Velocity Method

Concentration, 0.45%; PH, 6.8; thickness of cell, 0.60 cm.; interval between exposures, 30 min.; mean T, 294.2"; illumination, Hg lamp with Br_2 and Cl_2 filters; Imperial Process photographic plates

Sedimentation time, hrs [a]	AX, cm.	X, med., cm.	ω med.	$S_{20°}$, cm./sec. $\times 10^{-13}$
1	0.072	4.754	2573.0	12.40
1.5	.076	4.828	2481.8	13.84
2	.075	4 903	2471.7	13.57
2.5	.081	4.981	2597.1	13.06
3	.090	5.067	2586 6	14.38
3 5	.090	5.156	2544.7	14.60
4	.084	5 244	2523.7	13.62
			Mean	13.64×10^{-13}

[a] Sedimentation curves bear the same number in Fig. 5 as in these data.



$S = 13.64 \times 10^{-13}$; $D = 3.56 \times 10^{-7}$; $M = 373,400$.

Fig. 5.

Sedimentation Equilibrium Method.—In this method the molecular weight is given by the relation

$$M = \frac{2RT \ln (C_2/C_1)}{(1 - V\rho)\omega^2(X_2^2 - X_1^2)}$$

where C_1 and C_2 represent the protein concentrations at the distances X_1 and X_2, respectively, from the center of rotation. The other symbols have the usual significance.

The optical system as regards light source, filters, photographic plates, developer, etc., was the same as previously used. Photographs were taken with three different lengths of exposure time in order to obtain suitable photographic densities at all concentration levels within the cell for comparisons in the microphotometer. Changes in the intensity of illumination were corrected for by photographing a potassium chromate solution of suitable concentration at the same time as the protein solution. The potassium chromate solution was contained in a cell counterbalancing the cell containing the protein solution, and was masked off from the light source by a brass disk, except for a small window cut in the disk at an appropriate height above the level of the protein solution in the opposite cell.

In Table V are given data on a typical sedimentation equilibrium run with the acid–alcohol soluble protein. The mean molecular weight as shown by this run was 374,210. A duplicate run gave a mean value of 377,795.

TABLE V

ACID–ALCOHOL SOLUBLE CASEIN. SEDIMENTATION EQUILIBRIUM METHOD

Initial concentration, 0.50%; PH, 6.8; thickness of cell, 0.80 cm.; T, 293"; speed, 2986.6 r.p.m. ($\omega = 99.557$ r); equilibrium time, 66 hrs.; illumination, Hg lamp with Br_2 and Cl_2 filters; Imperial Process photographic plates

X_2, cm.	X_1 cm.	C_2, %	C_1, %	M
5.81	5.76	0.8050	0.7190	389,200
5.76	5.71	.7190	.6465	369,300
5.71	5.66	.6465	.5800	380,460
5.66	5.61	.5800	.5225	369,190
5.61	5.56	.5225	.4715	366,490
5.56	5.51	.4715	.4250	373,770
5.51	5.46	.4250	.3830	378,050
5.46	5.41	.3830	.3465	367,230
			Mean mol. wt.	374,210

The value of the molecular weight calculated from the protein concentrations at different distances from the axis of rotation was identical within the limits of error with those calculated from the sedimentation velocity method. These results are summarized in Table VI. The mean value of the molecular weight was found to be 375,256 ± 11,000.

TABLE VI

SUMMARY OF MOLECULAR WEIGHT VALUES FOR ACID–ALCOHOL SOLUBLE CASEIN

Method	Init. concn., %	Mean speed, r.p.m.	Mol. wt.
Sedimentation velocity	0.45	25,000	373,420
Sedimentation velocity	.32	43,950	375,600
Sedimentation equilibrium	.50	2,986	374,210
Sedimentation equilibrium	.50	2,972	377,795
		Grand mean	375,256

Discussion of Results

The experiments described in this paper with casein precipitated from cow's milk by Hammarsten's method have shown that this material is a mixture of several protein molecules of different weight, From 13 g. of this mixture we have separated and reclaimed 4.34 g. of protein by extraction with warm acidified 70% alcohol. This represented at least 33% of the original material and was found to be a definite chemical entity having a molecular weight of 375,000. It might be possible to obtain more than 33% of this protein from Hammarsten casein, as we have only performed the extraction twice, each time removing about the same amount of protein. On the other hand, the shape of the curves in Fig. 2, compared with the curves of other proteins studied in this Laboratory, indicates that, provided the extinction coefficient is the same for all of the protein molecules in Hammarsten casein, there can hardly be present as much as 33% of a protein possessing a molecular weight of 375,000 in Hammarsten casein. If this were the case, one would expect to find two distinct breaks in the upper parts of these sedimentation curves.

It might be argued that by the extraction process we have definitely changed the casein into some polymerized substance which was not originally present in the Hammarsten casein. In support of this argument we find the experiments of Robertson,[24] who concluded from ionic mobility experiments that potassium caseinate polymerized in the presence of 70% alcohol. It is quite possible, however, that compounds of casein with acid would behave differently with respect to alcohol than compounds of casein with base.

According to the experiments of Linderström-Lang[12,13] the polymerization argument seems to be untenable, for continued extractions eventually reach a point where no great amount of protein is further dissolved. This would not be the case were we dealing with a progressive polymerization.

Our own experiments were not designed to show which of the above views was correct. Our only aim was to ascertain whether a definite chemical entity was obtained by the extraction process. The matter would seem to hinge on whether, after continued extractions, the remaining product possessed the same solubility in fresh solvent as it exhibited in the beginning.

The particle size of the acid–alcohol soluble casein may be calculated from the specific sedimentation velocity data using Stokes' Law, under the assumption that the particle is spherical. This gives the value $r = 4.177 \times 10^{-7}$ cm. Using the diffusion constant, we can also calculate the particle size from Einstein's Law without making any assumption as to the shape of the particle. This gives the value $r = 5.994 \times 10^{-7}$ cm. From these values we conclude that the protein particle must be of some other shape

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[24] Robertson, "Physical Chemistry of the Proteins," T. B. Robertson, New York and London, 1918, p. 268.

than spherical. The ratio between the two values for the particle radius given by the two laws (r_E/r_S) is 1.43. This compares well with similar ratios already obtained in the cases of hemoglobin, serum albumin, serum globulin and phycocyan. This probably means that the departure of the particle from a spherical shape is about the same amount for all of these proteins.

Summary

1. Casein prepared by the Hammarsten method has been examined at Ph 6.8 in phosphate buffer solution by the centrifugal sedimentation velocity method and found to consist of a mixture of protein molecules of different weight.

2. Hammarsten casein was extracted with hot acidified 70% alcohol and the soluble protein precipitated out with dilute sodium hydroxide. This protein after washing was dissolved in phosphate buffer solution of Ph 6.8. Various concentrations were examined by both the sedimentation velocity and sedimentation equilibrium methods.

3. It was found that within the limits of experimental error the acid–alcohol soluble protein was homogeneous with regard to molecular weight and that it therefore probably was a pure chemical individual.

4. The molecular weight was found to be 375,000 ± 11,000.

5. The molecule was not spherical and deviated from the spherical shape by about the same amount that has been found for several other proteins.

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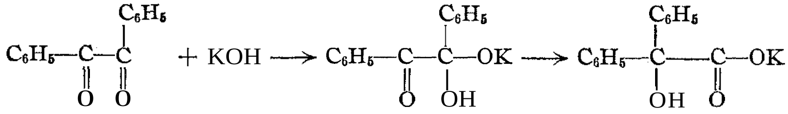
THE BENZILIC ACID REARRANGEMENT

BY THEODORE W. EVANS AND WILLIAM M. DEHN

RECEIVED JULY 1, 1929 PUBLISHED JANUARY 8, 1930

It seems probable that the benzilic acid rearrangement is best formulated as follows



$$C_6H_5-\underset{\overset{\|}{O}}{C}-\overset{C_6H_5}{\underset{\overset{\|}{O}}{C}} + KOH \longrightarrow C_6H_5-\underset{\overset{\|}{O}}{C}-\overset{C_6H_5}{\underset{OH}{C}}-OK \longrightarrow C_6H_5-\overset{C_6H_5}{\underset{OH}{C}}-\underset{\overset{\|}{O}}{C}-OK$$

The addition of one molecule of potash was postulated by Hoogewerff and van Dorp;[1] the migration of both C_6H_5 and H, by Michael;[2] ex-

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[1] Hoogewerff and van Dorp, *Rec. trav. chim.*, **9**, **225 (1890)**. These authors assumed that Ph and OK migrate from one carbon atom to the other.

[2] Michael, THIS JOURNAL, 42, **814 (1920)**. Michael assumes the addition of one mole of potassium hydroxide, and this forms a system which "may now completely convert itself, by the transmigration of phenyl and hydrogen, into a salt of the relatively strong benzilic acid."

perimental indication of $C_{14}H_{10}O_2 \cdot KOH$ was given by Scheuing.[3] It has been assumed that benzil adds to H_2O,[4] to $2H_2O$,[5] to 2KOH,[6] or to KOH.[7] Since it is possible to avoid water[8] and to limit the alkali to one molecule, it is possible to obtain definite proof not only that water is not necessary but that the intermediate additive[9] compound is formed.

All experiments directed toward increasing the yield of the acid have involved large excesses[10] of alkali. Experiments of only theoretical interest have always involved either water alone, or alkali alcoholate alone, or alcoholic potash, or mixtures of these. In no case has only one molecule of benzil, one molecule of potash and an indifferent solvent such as ether, benzene, etc., been employed. We have treated equivalents of benzil, furil and diacetyl with potash in anhydrous ether and have found that only one molecule of potash is necessary for the transformation.

A single lump of potassium hydroxide weighing 1.4 g., placed in absolute ether with 5.4 g. of benzil and shaken occasionally during four days, was replaced by 5.6 g. of a powdery, light yellow solid; the ether yielded 1 g. of unchanged benzil, melting at 95°. The solid was analyzed.

Anal. Calcd. for $C_{14}H_{10}O_2 \cdot KOH$: K, 14.68. Found: K, 15.04.

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[3] Scheuing, *Ber.*, 56, 252 (1923); 57, 1963 (1924). Schonberg, *ibid.*, 58, 235 (1925), criticizes Scheuing's product as affording no proof of an intermediate compound, "da das Anlagerungsproduct weder analysiert noch sein molekular gewicht bestimmt worden ist."

[4] Nef, *Ann.*, 298, 372 (1897). For a criticism of Nef's interpretation see Michael, THIS JOURNAL, 42, 812 (1920).

[5] Lachman first assumed the addition of two molecules of water but later assumed only one molecule of water. *Cf.* THIS JOURNAL, 44, 330 (1922), and 45, 1509, 1522, 1529 (1923); 46, 779 (1924). His contention that a mobile hydroxyl group shifts, that water is necessary for the benzilic acid rearrangement and his use of the word "metakliny," involving intramolecular oxidation and reduction, seem unjustified.

[6] Tiffeneau, *Rev. gen. sci.*, 585 (1907). Staudinger and Binkert, *Helv. Chim. Acta*, 5, 703 (1922).

[7] Schroeter, *Ber.*, 42, 2336 (1909), also assumed initial addition of one mole of potassium hydroxide, but his theory of rearrangement, involving the intermediate formation of diphenylketene was disproved by Nicolet and Pelc, THIS JOURNAL, 43, 935 (1921); see also Schonberg and Keller, *Ber.*, 56, 1638 (1923).

[8] Lachman states unequivocally that water is necessary for the benzilic acid rearrangement; see especially THIS JOURNAL, 46, 781 (1924). Others who have observed the effects of water are Jena, *Ann.*, 155, 78 (1870); Klinger, *Ber.*, 19, 1868 (1886).

[9] Scheuing used equivalents of alcoholic potash and benzil in ether solution and obtained a light yellow solid which he claimed was changed gradually at 0° and rapidly at 80° to potassium benzilate.

[10] From 3 to 8 equivalents of potassium hydroxide have been used. Liebig, *Ann.*, 25, 27 (1838); Zinin, *ibid.*, 31, 329 (1839); Limpricht and Schwandert, *Ber*, 2, 134 (1869); Jena, *Ann.*, 155, 79 (1870); Fischer, *Ber.*, 14, 326 (1881); Klinger, *ibid.*, 22, 1212 (1889); H. v. Liebig, *ibid.*, 41, 1644 (1908); Staudinger, *Ann.*, 356, 71 (1907); "Organic Syntheses," Vol. I, 1921, p. 29; Scheuing, *Ber.*, 56, 255 (1923); Schonberg and Keller, *ibid.*, 56, 1640 (1923).

Some of this salt, treated with concentrated sulfuric acid, gave the characteristic red color which benzilic acid does.[11] Upon acidifying 4.64 g. of this potassium benzilate, 3.71 g. (94%) of white needles of benzilic acid melting at 150° were obtained. Since no benzaldehyde or benzoic acid was detected, the precipitate represented an 81% transformation to potassium benzilate. The transformation was effected in the absence of water and while the additive compound was in the solid state. In another experiment equivalents of materials were ground up in a mortar under dry ether, but owing to rise of temperature or unavoidable contact with atmospheric moisture and oxygen, the yield was poor and contained benzaldehyde and benzoic acid.

From anhydrous ammonia, benzil and toluene was obtained a white solid, which proved to be benzilam,[12] melting point at 110°. With anhydrous ammonia, benzil and ether a white solid melting at 158° was obtained. With potash, it yielded ammonia and a white solid, insoluble in water, and melting at 203°. It will be further investigated.

When 5 g. of furil and 1 g. of sodium hydroxide in dry ether were shaken during twenty-four hours, 5.33 g. (88%) of a dark brown powdery mass was obtained.

Anal. Calcd. for $C_{10}H_6O_4 \cdot NaOH$: Na, 10.00. Found: Na, 10.27.

Acidification of the salt and extraction with ether yielded white needles of furilic acid agreeing in all properties with Fischer's product.[13]

With 10 g. of diacetyl and 6.5 g. of potassium hydroxide in dry ether, an immediate blackening of the potash resulted; the final sticky mass was brown-black, and though it contained acetaldehyde, resin, acetic acid and other products, it could not be made to yield dimethylglycolic acid.

Summary

One molecule of potash transforms benzil to benzilic acid; water is not necessary for this reaction. An additive compound is first formed which undergoes molecular rearrangement while in the solid phase.

SEATTLE, WASHINGTON

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[11] We have observed that 60% perchloric acid and 85% phosphoric acid also give red colorations with benzilic acid.

[12] Laurent, *J. prakt. Chem.*, [1] 35, 461 (1846).

[13] Fischer, Ann., 211, 222 (1884).

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

THE KINETICS OF THE REACTION OF HEXAPHENYLETHANE WITH OXYGEN

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Introduction

Gomberg and others have shown that hexaphenylethane when dissolved in non-ionizing solvents such as ether, benzene, toluene and carbon tetrachloride exists in at least two forms, undissociated hexaphenylethane and the free radical triphenylmethyl. The solutions are amber-colored, and it appears to be proved conclusively that the color is due to the free radical, part or all of which may be colored. When the amber-colored solution of hexaphenylethane in these solvents is shaken with air or oxygen, the color decreases very rapidly, the solution becoming colorless if the hexaphenylethane is sufficiently pure. A few moments after the shaking is stopped, the color reappears, but much more slowly than it disappeared. The over-all reaction in this process is

$$(C_6H_5)_3C—C(C_6H_5)_3 + O_2 \longrightarrow (C_6H_5)_3C—O—O—C(C_6H_5)_3$$

This simple experiment suggests that there is some colored substance in the solution before the addition of oxygen which is in equilibrium with hexaphenylethane, and that this substance reacts with oxygen to form triphenylmethyl peroxide at a much faster rate than that of the reaction through which it is in equilibrium with hexaphenylethane.

Again, the color of hexaphenylethane solutions decreases on dilution to a less extent than that predicted by Beer's law.[1] Hence the colored substance is formed by a reversible dissociation.

These two experiments together show that hexaphenylethane dissociates to form a colored substance, triphenylmethyl, whose reaction with oxygen can be much faster than its recombination. When such a condition exists, the kinetics of the over-all reaction are those of the preliminary slower step. Thus in this case the rate of oxidation of hexaphenylethane by this mechanism has to be that of its dissociation and is independent of the concentration of oxygen. That the necessary condition of rapid reaction of triphenylmethyl with oxygen can be achieved may be seen from the following considerations. The color of a hexaphenylethane solution can easily be reduced to less than one-tenth of its original depth by shaking with air or oxygen. Under these conditions the rate of re-combination, a bimolecular reaction, is reduced to less than 1% of its value in the oxygen-free solution, while that of dissociation is presumably unchanged. Consequently, practically all of the molecules which dissociate react with oxygen and very few of them return to the original hexaphenylethane. This failure of the

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[1] J. Piccard, *Ann. chim.*, **381**, **347** (1911).

intermediate to return to the original state is the necessary condition that a preliminary step shall be the rate-determining reaction.

It is, therefore, of interest to study the kinetics of the absorption of oxygen by hexaphenylethane solutions, for in this way the rate of the dissociation will be measured, or it will be possible to show that there is some other mechanism for the reaction.

In such measurements it will be necessary that the passage of oxygen from the gas phase to the liquid does not delay the reaction. Therefore, the solutions must be shaken sufficiently vigorously to permit this transfer of oxygen to occur at a rate much faster than that of the oxidation. In our measurements concordant results were obtained over periods during which the rate of passage of oxygen from the gas to the liquid varied thirty-fold. Again, in the beginning of each experiment, while the solvent was being saturated with oxygen and the free radical was being reduced below its equilibrium concentration, the rate of transfer of oxygen across the gas–liquid interface was often two hundred times as fast as the rate of absorption of oxygen at stages of the run during which significant measurements were being made. These two observations, which can be seen by an inspection of the curves in Fig. 1, show that a sufficiently rapid solution of oxygen was achieved. Attempts were made to measure the rate of solution of oxygen in carbon tetrachloride under the conditions of the experiment, but it was found to dissolve too rapidly.

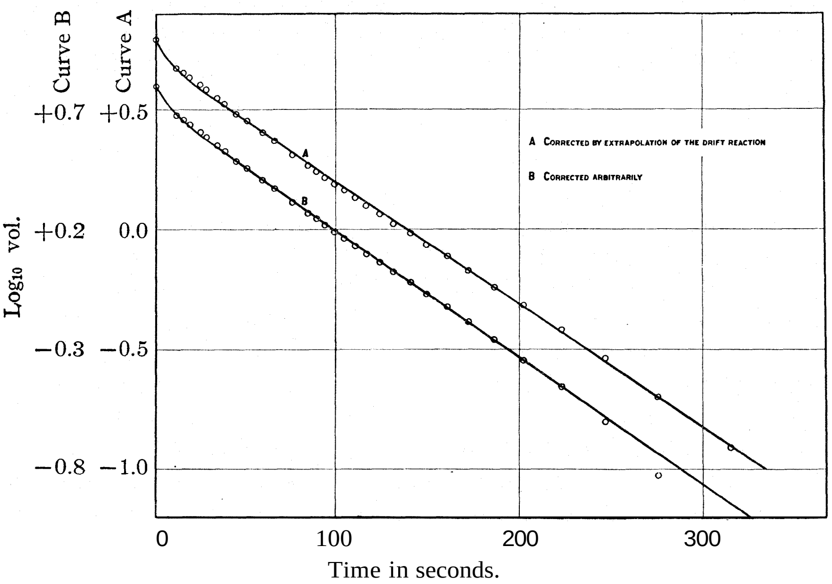

Fig. 1.—The logarithm of the volume of oxygen yet to be absorbed by hexaphenylethane plotted against the time.

The kinetics of the reaction was studied over ranges of temperature, of concentrations of hexaphenylethane and of partial pressures of oxygen. During any one run only the second variable changed. The solvent was carbon tetrachloride throughout. A few experiments were carried out in the presence of some of Bäckström's oxidation inhibitors.

Experimental Method

The method consisted of shaking hexaphenylethane solutions in the presence of oxygen gas mixed with nitrogen and measuring the rate of absorption of the gas.

The reaction was carried out in a vessel connected to a powerful automatic shaker, the whole being immersed in a thermostat. The volume of the containing vessel was so large, compared to that of the gas absorbed, that the composition of the oxygen and nitrogen mixtures used did not change significantly during an individual experiment.

The reaction vessel was attached by a rubber connection to a long calibrated horizontal tube which was bent at the end and dipped into a basin of liquid. This tube served as a constant pressure gas buret.

During an experiment the liquid meniscus advanced along the buret, and as it passed the calibration marks the time was registered. This was done by pressing a key which sent sparks through a paper tape moving at a known and constant rate. After the run had been made, the times were calculated from the distances between the marks burned through the tape.

Owing to its length, the buret was not immersed in the thermostat, but was surrounded by a jacket through which water flowed. In order to have an evenly moving meniscus, water was used as the buret liquid.

A certain amount of difficulty was encountered owing to the violent shaking which caused vibrations of the meniscus in the buret. This trouble was entirely overcome. In its final construction the apparatus could be shaken without causing any appreciable fluctuations of the meniscus in the buret.

A temperature of 0° was maintained in the thermostat by a mixture of ice and water. On account of the excellent stirring no variation in temperature as large as a tenth of a degree could be observed. For temperatures below 0° alcohol was added to the above mixture. In such experiments the temperatures increased a couple of tenths of a degree during the runs. These variations of temperature were measured. The observed volumes of gas were then corrected for this change of temperature from the known volume of gas in the reaction vessel and on the assumption that the change of temperature was proportional to the elapsed time. A few measurements were made above 0°. In these cases no device except insulation was used to keep the temperature of the thermostat constant. The rate of change of the temperature was observed and the necessary corrections to the volumes applied.

The solutions of hexaphenylethane were made by shaking solutions of triphenylchloromethane with molecular silver. The whole process of preparation and siphoning away from the silver chloride into containers was done in an atmosphere of inert gas. These containers were sealed and put into the reaction vessel. The required mixture of oxygen and nitrogen could then be introduced and the whole apparatus allowed to come to temperature equilibrium. When the shaker was started the sealed container was broken and the solution came into contact with the gas. A forward motion of the meniscus showed when this occurred.

Results at Constant Oxygen Pressure and Temperature.—The motion of the meniscus in the gas buret presented three phases, which appeared clearly differentiated to an observer of the experiment. The initial phase was a very rapid advance, that is, absorption of gas, starting the moment the sample tube broke and lasting about ten seconds. The second phase was a slower advance of the meniscus, decreasing in rate as the time increased. The second phase merged gradually into the final phase, which was a very slow advance continuing for more than an hour.

The interpretation of the rapid gas absorption during the initial phase was the process of saturating the carbon tetrachloride with oxygen as well as the reaction of the gas with that portion of the hexaphenylethane which existed at the start as the free radical.

The major portion of gas absorption takes place during the second phase, which represents the main reaction, the oxidation of hexaphenylethane.

The last phase is evidently not due to any reaction of hexaphenylethane, for the apparent half time of the second or main phase is about one minute, so that after ten minutes there should be practically no hexaphenylethane left; but the third phase continues noticeably for over an hour. Further, there is no combination of reactions of different orders but of the same substance which can account for both the second and final phases in the oxygen absorption, if reactions having ridiculous orders are excluded. On the other hand, the entire advance of the meniscus from twenty seconds after the start to the finish can be accounted for on the assumption that there are two substances present, one of which absorbs oxygen by a first order reaction whose half time is a little less than a minute, while the other compound is present in comparatively small quantities and reacts at a much slower rate, the half time of the second reaction being about a quarter of an hour.

In order to be sure that the main reaction is first order with respect to hexaphenylethane, it is necessary to correct for the side reaction. This may be done by extrapolating the measurements obtained during the latter part of the experiment, in order to calculate the absorption of gas by the impurity during the main part of the run.

The procedure is as follows: the experiment is continued until no more oxygen is absorbed, so that the volumes of oxygen yet to be absorbed may be obtained for any time at which a reading is made. The values of the logarithm of this quantity are plotted against the times and the best straight line is drawn through the points obtained ten minutes or more after the start. From the extension of this line to earlier times, the amount of oxygen which will be absorbed by the impurity may be read off. By subtracting this value from the total amount of oxygen yet to be absorbed, the volume of the gas yet to be absorbed by hexaphenylethane is obtained. This quantity is proportional to the concentration of hexaphenylethane. It may be noted that it is assumed that the side reaction is first order. The volumes involved are too small to decide this point, but for that very reason the assumed order is unimportant.

This method may be illustrated by a typical experiment, which was carried out at 0° and with 0.93 atmosphere of oxygen. The absorption of oxygen by the impurity near the end of the run is shown in Table I.

TABLE I

ABSORPTION OF OXYGEN BY THE IMPURITY

Time in minutes	0	10	15	20	25	30	35	40
Vol. to absorb, cc.	0.670	0.250	0.155	0.147	0.141	0.140	0.135	0.100
Time in minutes	45	50	55	60	65	70	75	80
Vol. to absorb, cc.	0.054	0.043	0.054	0.052	0.052	0.025	0.020	0.011
Time in minutes	85	90	95	100	105	110	115	120
Vol. to absorb, cc.	0.013	0.010	..	...	...	...	...	...

The volumes given in the second and fourth lines are calculated on the basis that the final reading is 6.770. The straight line which was drawn through the plot of the logarithms of these values against time corresponded to a total volume of 0.49 cc. absorbed by the impurity and a rate constant of 0.044 reciprocal minutes.

Other experiments agreed approximately with this one, that is, somewhere between 5 to 15% of the oxygen taken up was absorbed by a reaction whose half-time was approximately a quarter of an hour.

In Table II the first two columns show the times and the volumes of oxygen yet to be absorbed. Column 3 is the extrapolation of lines two and four of Table I. The volumes of oxygen yet to be absorbed by hexaphenylethane are exhibited in the fourth column.

TABLE II

ABSORPTION OF OXYGEN BY HEXAPHENYLETHANE

Time, sec.	Total cc. to be abs.	To be abs. by impurity, cc.	To be abs. by hexaphenylethane, cc.	Same as Col. 4 but obt. by appros. method
0	6.70	0.49	6.21	6.25
11.1	5.19	.49	4.70	4.74
15.3	4.99	.49	4.50	4.54
18.9	4.79	.49	4.30	4.34
24.7	4.49	,48	4.01	4.04
28.2	4.30	.48	3.82	3.85
34.0	4.00	.48	3.52	3.55
38.3	3.80	.48	3.32	3.35
44.9	3.50	.48	3.02	3.05
50.5	3.30	.47	2.83	2.85
59.4	3.00	,47	2.53	2.55
65.8	2.79	.46	2.33	2.34
76.0	2.50	.46	2.04	2.05
84.6	2.30	.46	1.84	1.85
89.5	2.20	.46	1.74	1.75
93.9	2.10	.46	1.64	1.65
99.2	2.00	0.46	1.54	1.55
104.7	1.90	.45	1.45	1.45
110.5	1.80	.45	1.35	1.35
117.0	1.70	.45	1.25	1.25
124.0	1.60	.45	1.15	1.15
131.5	1.50	.45	1.05	1.05
140.4	1.40	.44	0.96	0.95
149.4	1.30	.44	.86	.85
160.9	1.20	.43	.77	.75
172.3	1.10	.43	.67	.65
186.1	1.00	.43	.57	.55
202.0	0.90	.42	.48	.45
222.5	.80	.42	.38	.35
245.2	.70	.41	.29	.25
275.3	.60	.40	.20	.15
315.0	.50	.376	.124	.05

In Pig. 1, Curve A, the logarithms of the volumes of oxygen yet to be absorbed by hexaphenylethane are plotted against the times. In this figure the curve from twenty-five seconds onward is a ruled line whose slope corresponds to a rate constant equal to 0.0118 reciprocal seconds. It can thus be seen that the reaction is quite strictly first order with respect to hexaphenylethane over a thirty-fold change of the concentration of that substance.

This method of calculating the rate constant was carried out for several runs at 0°, but it could not be used at other temperatures, because the thermostat could not be held sufficiently constant in temperature to permit an approximate evaluation of the effect of the side reaction; therefore, another method of correction was used. This was based on the knowledge previously obtained that the main reaction is strictly first order with respect to hexaphenylethane.

This second way of correcting for the side reaction consists of subtracting such a constant amount from the observed values of oxygen yet to be absorbed, that their logarithms fall on a straight line when plotted against the time. Thus in the experiment shown in Tables I and II, if 0.45 cc. is subtracted from the amounts of oxygen yet to be absorbed, the resulting values, which are shown in Col. 5 of Table II, are such that their logarithms when plotted against the time fall on a straight line from about 25 to 220 seconds. This can be seen on inspection of Curve B of Fig. 1. In this drawing the curve from twenty-five seconds onward is a ruled line whose slope corresponds to a rate constant of 0.0122 reciprocal seconds. This value agrees fairly well with 0.0118, obtained by the logically more correct first method.

The second method is only applicable when the drift reaction contributes only a small fraction to the rate of absorption of oxygen. Thus in the present experiment between the times 50.5 and 160.9 seconds 0.04 cc. of oxygen was absorbed by the impurity and 2.06 cc. by the hexaphenylethane. As this proviso will not hold near the end of the reaction, the approximate method cannot be extended over as great a range as the other. This can be seen by comparing Curves A and B of Fig. 1.

The approximate method introduces an uncertainty of about 10% into a measurement, owing to the fact that it is possible to choose a range of values for the correcting volume which will make the significant measurements correspond to a first-order reaction. This uncertainty increases as the accuracy in the determined volumes of gas decreases. The uncertainties introduced by extrapolation of the side reaction are less.

Owing to the somewhat large errors introduced in the way described above, a great many experiments were performed. All the chief points discussed in the text are based on averages of more than forty individual experiments.

Throughout the rest of the text the rate of change of the logarithm of the concentration of the hexaphenylethane under otherwise constant conditions will be referred to as the rate constant for those conditions, and will be represented by the letter K. The actual values given will be those obtained by the approximate method of correction. The units are reciprocal seconds.

Variation of Rate Constant **with** Oxygen Pressure.—The results obtained by changing the partial pressure of oxygen but keeping the temperature constant at 0° are shown in Table III.

It will be noticed that K changes considerably with change of the partial pressure of oxygen. Conant and Evans[2] have published measurements of the rate of the reactions of several dixanthyls with oxygen. They have shown that the rate of absorption of oxygen by these substances is inde-

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[2] Conant and Evans, THIS JOURNAL, 51, 1925 (1929).

TABLE III

VARIATION OF KATE CONSTANT WITH OXYGEN PRESSURE

Partial pressure of oxygen, atm.	No. of observations	Rate constant Av., 1/sec.	Rate constant Av. dev., 1/sec.
0.93	17	0.0124	±0.00071
.80	4	.0118	.00005
.60	4	.0105	.0003
.55	5	.0104	,0003
.43	3	.00989	.0003
.31	3	.00837	.00029
.20	11	.00735	.00017

pendent of the oxygen pressure. This difference in the kinetics of the oxidation of hexaphenylethane and of the related dixanthyl is not surprising as it is accompanied by a thousand-fold change in the rate constants and more than 10,000 calorie change in the heat of activation.

It has been shown in the introduction that hexaphenylethane can absorb oxygen by a reaction whose rate is independent of the oxygen pressure. Consequently there must be a second mechanism for the oxidation of hexaphenylethane.

The alternatives for this mechanism are either a reaction of an undissociated but active form of hexaphenylethane, or a dissociation into an isomer of triphenylmethyl, followed by a combination with oxygen. This second form must, however, be colorless, and it must recombine more rapidly than it reacts with oxygen. This latter alternative agrees with the suggestion of Gomberg and Sullivan[3] that triphenylmethyl exists in two forms, which differ in color. However, the authors favor the first alternative on account of its greater simplicity. The experimental results can be equally well explained, whether the oxygen combines with a colorless free radical or with an active but undissociated form of hexaphenylethane. We shall in future refer to the second mechanism as the direct oxidation.

If the values of K are plotted against the pressure of oxygen the points seem to fall on a curved line. This is shown in Fig. 2, in which Curve A is the best parabola and Curve B is the best straight line.[4]

The equation for the straight line is $K = 0.00628 + 0.00678\ P_{O_2}$. This equation means that there are two independent mechanisms. One of these is independent of the oxygen pressure, and has a rate constant equal to 0.00628 reciprocal seconds. Its rate is that of the dissociation into free radicals. The rate of the other reaction is proportional to the oxygen pressure. Its rate constant is 0.00678 in reciprocal seconds and reciprocal atmospheres.

The equation of the parabola is $K = 0.00511 + 0.01225 P_{O_2} - 0.004715 P_{O_2}^2$. The probable percentage error calculated for the coefficient of $P_{O_2}^2$

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[3] Gomberg and Sullivan, THIS JOURNAL, 44, 1822 (1922).

[4] These curves are the most probable of their respective types, taking all the values given in Table III into consideration, but the circles represent mean values.

is 23.3%. The value of this coefficient is, therefore, more than four times the probable error, which formally means that the curvature is real. However, the calculation of probable error does not take into account any consistent error. Thus although the passage of oxygen across the gas–liquid interface was sufficiently rapid to eliminate any large errors, it is possible that the small curvature of the plot may be due to a slight delay involved in this process. However, having given this warning, we shall treat the curvature as significant.

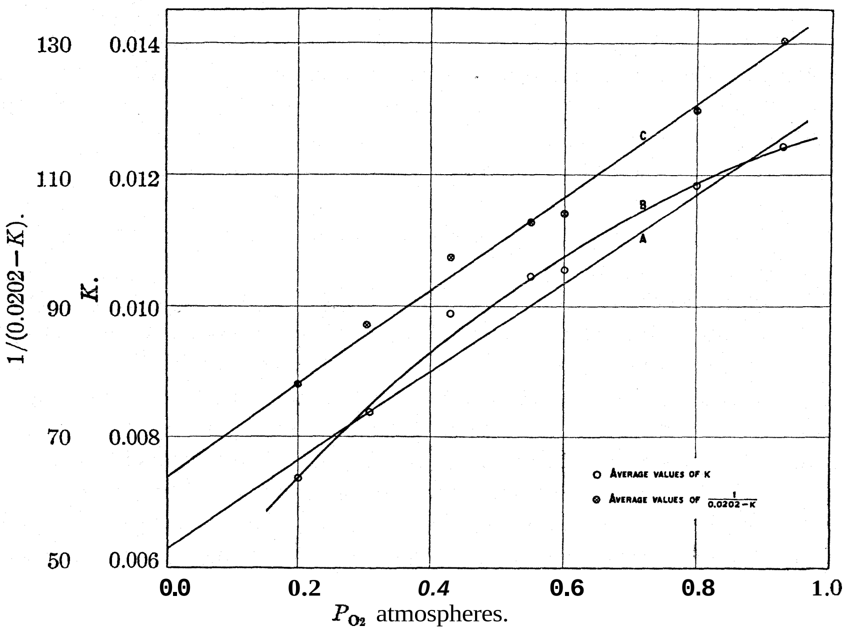

Fig. 2.—Variation of the rate constant with oxygen pressure.

This curvature could be explained by assuming that there are two independent mechanisms. One of which has a rate independent of the oxygen pressure and the other has a rate proportional to a fractional power of the oxygen pressure. The measurements would indicate that this fractional power is the square root. However, it would be necessary to assume an unlikely mechanism in order to account for the proportionality between the reaction rate and the square root of the oxygen pressure.

It is more probable that the direct oxidation is first order with respect to oxygen. The curvature may then be due to the formation of an active intermediate whose rate of return to the normal form is near that of its oxidation. In such a case the intermediate reaches a steady state during the reaction, and its concentration depends, not only on the concentration of hexaphenylethane, but also on the rate of oxidation. If the dissociation depends on the same active intermediate, the steady state depends on the summed effects of the two mechanisms. In both cases the mathematical expression for the kinetics is $K = K_0 - 1/(a + bP_{O_2})$. In the next paragraph we have derived this equation for the more complex case.

Let P_1, P_2 and P_3 represent the specific rate constants of the reactions of active hexaphenylethane to normal hexaphenylethane, of dissociation, and of reacting directly with oxygen, respectively. The probabilities that the life of an individual among these active forms is eventually terminated by each of these processes are, respectively

$$\frac{P_1}{P_1 + P_2 + P_3P_{O_2}} \qquad \frac{P_2}{P_1 + P_2 + P_3P_{O_2}} \qquad \frac{P_3P_{O_2}}{P_1 + P_2 + P_3P_{O_2}}$$

The sum of these probabilities is unity.

$$\frac{P_1}{P_1 + P_2 + P_3P_{O_2}} + \frac{P_2 + P_3P_{O_2}}{P_1 + P_2 + P_3P_{O_2}} = 1$$

If the steady state concentration of the active form is small compared to the concentration of the normal form, the rate of formation of the intermediate is equal to that of its decay. If K_0 is the rate constant for its formation

$$K = K_0\left(\frac{p_2 + p_3P_{O_2}}{p_1 + p_2 + p_3P_{O_2}}\right) = K_0 - \frac{p_1}{p_1 + p_2 + p_3P_{O_2}}K_0$$

Replacing $p_1 + p_2/(p_1K_0)$ and $p_3/(p_1K_0)$ by the constants a and b, respectively, $K = K_0 - 1/(a + bP_{O_2})$.

The constants in this equation can be obtained from the experimental values by a graphical method. The equation is expressed in the form $1/(K_0 - K) = a + bP_{O_2}$. Various values are assumed for K_0, in order to find the range of values for which the quantity $1/(K_0 - K)$ is a linear function of P_{O_2}, within the experimental accuracy of the determinations of K and P_{O_2}. The range of values found was not very great, and the mean value, 0.0202 reciprocal seconds, was chosen for K_0. Curve C in Fig. 2 is this graph. The slope of the line $1/(K_0 - K)$ is b, and its intercept with the ordinate is a. The values found are $a = 64$ seconds and $b = 71$ seconds times reciprocal atmospheres.

The rate of the dissociation reaction is $K_1 - (1/a)$, whether or not the two mechanisms depend on the same intermediate. The value = 0.0046 reciprocal seconds. This compares favorably with 0.0051, the value obtained by extrapolating the parabola to $P_{O_2} = 0$. If the two mechanisms depend on the same intermediate, its rate constant of formation is K_0; but if this substance is only involved in the direct oxidation, the constant is equal to $1/a$.

There are thus three possible theories of the kinetics of the mechanism of the reaction which we have called the direct oxidation. The first is that this reaction is strictly first order with respect to oxygen. The second is that it depends on an intermediate form of hexaphenylethane whose concentration is kept below its equilibrium value. The third is that the substance which is held in a steady state is an intermediate in both the dissociation and direct oxidation. The actual results favor the second and third hypotheses, but these two are not experimentally distinguishable, as they correspond to the same mathematical expression for the variation of K with P_{O_2}.

No matter which theory of the kinetics is correct, a considerable fraction of the reactions occurs through the mechanism of direct oxidation, when oxygen at one atmosphere is used. These fractions may be calculated. They are approximately $^1/_2$, $^3/_4$ and $^5/_6$ on the first, second and third assumptions, respectively.

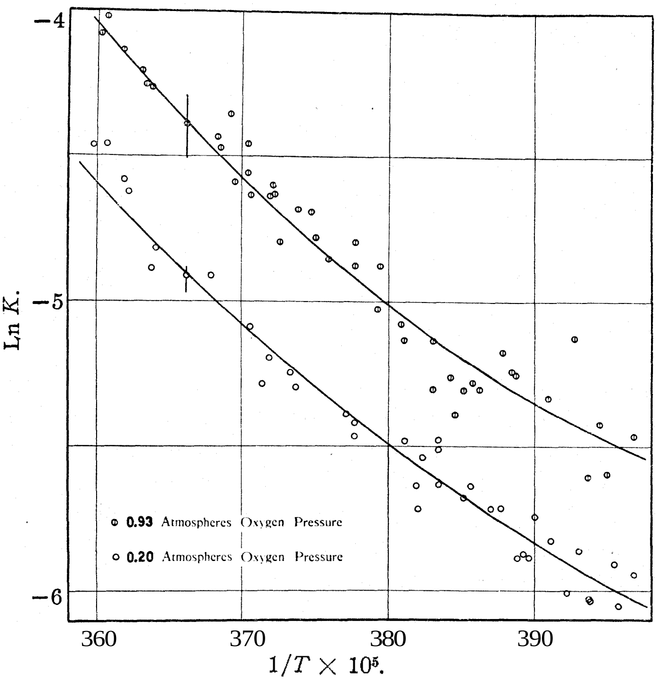

Fig. 3.—Variation of the natural logarithm of the rate constant with the reciprocal of the absolute temperature.

Variation **of** K with **Temperature.**—The rate constants with 0.93 and 0.20 atmospheres of oxygen were measured from 5 to −21°. **A** large number of experiments were performed, and the logarithms of the results were plotted against the reciprocal of the temperature. By means of a least square method of reduction of the data the most probable parabolas were calculated. These parabolas and the individual data are shown in Fig. **3.** Only the average values of ln K at 0° are shown, as the complete data for K at 0° may be found in Table III. The complete data are given in Tables IV and V.

TABLE IV

RATE CONSTANTS AT 0.93 ATMOSPHERE OF OXYGEN

T	K	T	K	T	K
4.45	0.0169	0.00	0.0122	− 9.35	0.00655
4.25	.0179	.00	.0127	− 9.55	.00759
3.25	.0160	.00	.0133	−10.4	.00622
2.33	.0153	.00	.0112	−10.6	.00589
2.2	.0133	−1.6	.0119	−12.0	.00497
2.05	.0142	−1.7	.0114	−12.0	.00589
1.75	.0141	−2.25	.0128	−12.8	.00519
0.00	.0115	−2.45	.0102	−13.0	.00455
.00	.0111	−3.1	.0116	−13.4	.00496
.00	.0111	−3.1	.0105	−13.85	.00507
.00	.0112	−3.3	.00971	−14.15	.00496
.00	.0132	−4.2	.00969	−15.2	.00566
.00	.0125	−4.35	.01005	−15.6	.00528
.00	.0134	−4.45	.00973	−15.75	.00523
.00	.0119	−4.75	.00825	−17.3	.00482
.00	.0123	−5.6	.00926	−18.35	.00592
.00	.0129	−6.25	.00917	−19.0	.00367
.00	.0126	−6.4	.00839	−19.6	.00440
.00	.0128	−7.1	.00781	−19.85	.00370
.00	.0135	−8.25	.00825	−21.1	.00422
.00	.0137	−8.25	.00759		

TABLE V

RATE CONSTANTS AT 0.20 ATMOSPHERE OF OXYGEN

T	K	T	K	T	K
4.8	0.01152	0.00	0.00743	−13.4	0.00342
4.15	.01155	−1.3	.00736	−13.8	.00355
3.25	.01024	−3.3	.00618	−14.7	.00328
3.0	.00984	−3.85	.00506	−15.15	.00328
2.55	.00957	−4.25	.00554	−15.9	.00277
1.75	.00756	−5.2	.00528	−16.15	.00281
1.55	.00810	−5.5	.00500	−16.45	.00278
0.00	.00736	−7.95	.00457	−16.7	.00320
.00	.00756	−8.35	.00422	−17.45	.00295
.00	.00747	−8.35	.00443	−18.15	.00246
.00	.00696	−10.7	.00416	−18.65	.00285
.00	.00751	−11.25	.00356	−19.1	.00240
.00	.00746	−11.3	.00329	−19.15	.00239
.00	.00751	−11.5	.00387	−20.2	.00272
.00	.00744	−12.25	.00357	−20.4	.00235
.00	.00696	−12.3	.00417	−21.1	.00262
.00	.00724	−12.3	.00404		

The equations for these parabolas are $Y = -0.03415 - 5890X + 4.98 \times 10^6X^2$ for 93% oxygen, and $Y = -0.5851 - 5220X + 3.45 \times 10^6X^2$ for 20% oxygen. In these equations $Y = \ln K + 4$, and $X = 1/T - 0.0036$. These curves are approximately parallel, almost to within the probable errors. Thus the probable errors in the coefficients of X are 207 and 261, respectively, while the difference between the coefficients is 670. The probable errors in the coefficients of X^2 are 0.569×10^6 and 0.707×10^6, respectively, and the difference between the coefficients is 1.53×10^6. The curvature appears to be real, for in the first equation the coefficient of X^2 is nearly nine times the probable error, and in the second the coefficient of X^2 is nearly five times the probable error. The curve for 93% oxygen was based on sixty-two measurements and that for 20% oxygen on fifty-two. The values of K at 0° calculated from these equations both differ by less than 2% from the average values obtained at this temperature.

The heat of activation of a reaction may be calculated from the rate of change of the logarithm of the velocity constant with the reciprocal of the temperature. The equation is blog, $K/\partial(1/T) = -E/R$. If such an equation is applied to the reaction of oxygen with hexaphenylethane, the calculated value of the heat of activation will depend on the temperature. Thus with 93% oxygen the apparent heat of activation is 10,500 calories at 0°, 8900 calories at $-6°$ and 4800 calories at $-20°$. With 20% oxygen the heats of activation at these temperatures are 9500, 8400 and 5500 calories, respectively. Since the changes of the heat of activation with temperature depend on the curvature of the plot of log K against $1/T$, this dependence of E on the temperature is presumably real.

Such a variation of the value of blog $K/\partial(1/T)$ with the temperature could be explained by the double mechanism of the reaction; but this would necessitate that the dissociation and direct oxidation have very different heats of activation. In this case the values of blog $K/\partial(1/T)$ would change markedly when the percentage of oxygen is varied, but the differences between the values for 93 and 20% of oxygen are only slightly in excess of the probable errors. One is, therefore, forced to the conclusion that this anomalous change of blog $K/\partial(1/T)$ with the temperature has nothing to do with the double mechanism of the reaction, but is a characteristic of both the dissociation and the direct oxidation, or that the result is due to some consistent experimental error. Of course, this is not the first time that the logarithm of a reaction rate has been found not to be a linear function of the reciprocal of the temperature.

It is not strictly correct on the activation theory of reactions to use the same equation for calculating the change of K with the temperature for both the dissociation and direct oxidation, for the latter is a bimolecular reaction. The proper equation for second-order rate constants is $\frac{\partial(\ln K - \frac{1}{2}\ln T)}{\partial(1/T)} = -\frac{E}{R}$, but the value of $\frac{1}{2}\frac{\partial \ln T}{\partial(1/T)}$ is smaller than the prabable errors. Also the variation of the rate of the direct oxidation with temperature is dependent on the rate of change of solubility of oxygen in carbon tetrachloride with temperature. This effect is also negligible.

It may be noted that the parallelism of the curves obtained with 93 and 20% of oxygen shows that the heats of activation of the dissociation and direct oxidation have nearly the same magnitudes.[5] This would suggest that little or no energy is needed to activate the oxygen. This to some extent confirms the view of G. N. Lewis that the electronic structure of oxygen is $:\underset{\cdot\cdot}{\overset{\cdot}{O}}:\underset{\cdot\cdot}{\overset{\cdot}{O}}:$, and as such does not require activation in order to react.

The Effect of Inhibitors.—Bäckström[6] has found that the absorption of oxygen by benzaldehyde in the dark is slowed down to a great extent by many substances. Diphenylamine, anthracene and phenol are notable examples of these inhibitors. The effects of these substances were tried. The inhibitors were used in concentrations of 0.005 molal, which is about one-fifth of the concentration of the hexaphenylethane. The two substances did not mix until the experiments were started by the breaking of the container for the hexaphenylethane. The experiments were carried out at 0° and at an oxygen pressure of 0.20 atmosphere. The diphenylamine and anthracene had no appreciable effect; with the former substance $K = 0.00693$ reciprocal seconds was the average of two experiments, and with the latter 0.00725 reciprocal seconds was the average of two experiments. The mean value of K obtained with pure carbon tetrachloride was 0.00735 reciprocal seconds. The value $K = 0.00693$ in the presence of diphenylamine is perhaps a little lower than what might be expected on pure chance; but in this case the diphenylamine was attacked, and much color developed in the solution. The absorption of any oxygen by the diphenylamine would tend to lower K on account of the approximate character of the method used to estimate the total volume of oxygen absorbed by the hexaphenylethane. For this reason it is best to consider the difference between 0.00735 and 0.00693 as experimental error.

With phenol an appreciable increase in the rate was observed. The average of two measurements was $K = 0.0110$ reciprocal seconds. This is more than a 50% increase in the rate, which is much greater than the probable experimental error.

Summary

Measurements were made on the rate of oxygen pressure by carbon tetrachloride solutions of hexaphenylethane under the conditions of constant temperature, of constant oxygen pressure and of vigorous shaking.

The experiments were carried out at many temperatures from 5 to $-21°$, and with several partial pressures of oxygen from 0.93 to 0.20 atmosphere.

The reaction rate was found to be proportional to the concentration of hexaphenylethane, and to a somewhat complicated function of the oxygen

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[5] Calculations which separate the two heats of activation greatly enhance the experimental error, so that "nearly" may be taken as equivalent to "within 3000 calories."

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

pressure. This function could be best expressed as $K_0 - 1/(a + bP_{O_2})$, in which K_0, a and b are constants.

The character of this function was explained on the assumption that there are two mechanisms, for the reaction. One of these is a dissociation into free radicals followed by a very rapid oxidation. The other is a direct oxidation. On these assumptions alone the function would be $a + bP_{O_2}$; its more complicated form was assumed to be due either to a consistent error, or to the formation of an active intermediate which is held in a steady state other than its true equilibrium ratio with normal hexaphenylethane.

The logarithm of the rate constant was found not to be a linear function of $1/T$. The calculated heats of activation increase with temperature, but are approximately constant to change of the oxygen pressure.

The reaction was not inhibited by diphenylamine, anthracene nor phenol. The last substance increased the rate.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 49]

THE RATE OF REACTION OF CERTAIN ALCOHOLS WITH PARA-NITROBENZOYL CHLORIDE IN ANHYDROUS ETHER SOLUTION

BY AVERY ALLEN ASHDOWN[1]

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The speed of ester formation from alcohols and p-nitrobenzoyl chloride, in ether solution, has been studied in this Laboratory as a means for measuring the relative reactivity of the hydroxyl hydrogen of the alcohols. In two earlier papers,[2] the influence of the structure of the alcohols on the rate of the reaction has been discussed.

Although the net result of the reaction consists in the formation of a molecule of hydrogen chloride and one of an ester, from one molecule each of alcohol and acid chloride, the second-order velocity constants decrease steadily as the reaction proceeds. This peculiarity was observed with all of the twenty-nine alcohols studied, and it is not dependent on the type of alcohol, whether primary, secondary or tertiary. Furthermore, if the original molal solutions are replaced by half-molal ones, the second-order constants are much smaller and, as before, decrease with the progress of the reaction. If the drop in the value of the second-order reaction constants were attributable to the non-ideality of solution alone,

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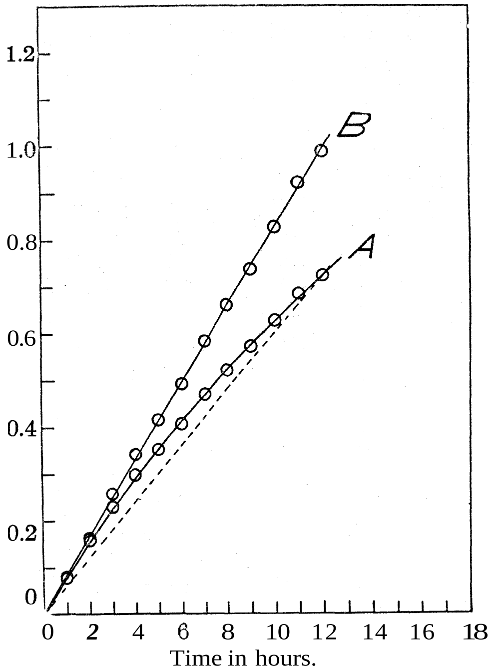
[1] Research Associate, Massachusetts Institute of Technology.

[2] (a) Norris and Ashdown, THIS JOURNAL, 47, 837 (1925); (b) Norris and Cortese, *ibid.*, 49, 2640 (1927).

then the half-molal solutions would be expected to give both a higher and a more steady value for the constant. The very reverse of this, found by experiment, led to a study of the law of the reaction rate as a possible means of throwing light on the mechanism involved,

At the outset, a graphical analysis of the data for methyl and ethyl alcohols showed that the reaction was of an order higher than second, probably of the third order. The integrated form of the second-order equation for equal molal concentrations, $KtC_0 = x/(1 - x)$, in terms of the fraction, x, of reactant transformed, is linear. Plotting values of $x/(1 - x)$ against t should give a straight line. In all cases, however, the data led to a smooth curve, bending toward the t-axis (Fig. 1, Curve A, n-butyl alcohol). The slopes of this curve, corresponding to values of the constant, K, are steadily decreasing. The following considerations show how the graphically observed change in K indicates a third-order reaction. For a second-order reaction between two compounds at equal concentrations



Pig. I.—Rate of reaction of *n*-butyl alcohol with *p*-nitrobenzoyl chloride. Curve **A**, data calculated as a second-order reaction. $x/(1 - x)$ plotted against t in hours. Curve B, data calculated as a third-order reaction. $x(2-x)/2(1 - x)^2$ plotted against t in hours.

$$dx/dt = k(1 - x)^2 \text{ or } dx/(1 - x)^2 = kdt$$

but

$$d\frac{(x)}{(1 - x)} = dx/(1 - x)^2 = kdt$$

In the case of a third-order reaction (equal concentrations), however

$$dx/dt = k(1 - x)^3 = k(1 - x)^2(1 - x)$$

In other words, for a third-order reaction

$$d(x/1 - x) = k(1 - x)dt$$

This equation obviously satisfies the condition observed graphically and strongly suggests a reaction of the third order.

In the light of this indication, the data on all twenty-nine alcohols were calculated using the third-order equation for equal molal concentrations. For all cases throughout a given run the constants thus obtained were steady, not decreasing as did the second-order constants. Furthermore, the half-molal solutions yielded third-order constants which were higher than those for molal solutions, a consequence to be expected if the reactions were of the third order, and the solutions not ideal. In Table I the second- and third-order constants for n-butyl alcohol are given as an example.

TABLE I

n-BUTYL ALCOHOL AND *p*-NITROBENZOYL CHLORIDE AT EQUAL MOLAL CONCENTRATIONS

Molal					Half molal				
t	x	K_2^1	K_3^1	K_3^0	t	x	$K_2^{0.5}$	$K_3^{0.5}$	K_3^0
1	0.0717	0.0772	0.080	0.119	1	0.0266	0.055	0.110	0.138
2	.1366	.0791	.085	.125	2	.0452	.047	.097	.121
3	.1877	.0770	.086	.124	3	.0727	.052	.107	.134
4	.2302	.0747	.086	.123	4	.0854	.047	.098	.121
5	.2614	.0708	.083	.119	5	.1035	.046	.098	.121
6	.2895	.0679	.082	.116	6	.1146	.043	.092	.114
7	.3212	.0675	.084	.117	7	.1366	.045	.098	.120
8	.3439	.0654	.083	.115	8	.1506	.044	.097	.117
9	.3663	.0638	.082	.113	9	.1632	.043	.095	.115
10	.3862	.0630	.083	.114	10	.1736	.042	.093	.114
11	.4071	.0624	.084	.115	11	.1840	.041	.091	.112
					12	.1963	.041	.091	.112

K_2^1 and $K_2^{0.5}$ are second-order and K_3^1 and $K_3^{0.5}$ are third-order constants at molal- and half-molal concentrations. K_3^0 is the third-order constant at infinite dilution, computed analytically. t = time in hours.

Curve B, Fig. 1, also shows how the data from n-butyl alcohol conform to a third-order reaction. The integrated form of the third-order equation, equal molal concentrations, in terms of the fraction, x, of reactant used is

$$KtC_0^2 = \frac{x(2-x)}{2(1-x)^2}$$

It should yield a straight line if the numerical value of the right-hand member of the equation be plotted against t.

Description of Experiments

When the calculation of the third-order constants was completed, the reaction rate was tested by a series of experiments. The method for measuring the rates and the details for purifying the compounds have been described rather completely in two previous papers.[2] The procedure consisted in dissolving the acid chloride in anhydrous ether contained in a glass-stoppered Erlenmeyer flask, placing the flask in a thermostat at 25°, adding alcohol equivalent to the acid chloride and following the rate by titrating the hydrogen chloride produced. All concentrations were in moles per thousand grams of ether.

In a modification of the method, equal volumes of the reaction mixture, measured from a buret, were sealed in small glass vials. These were placed in the thermostat and at appropriate intervals a vial was taken out and the entire contents titrated for hydrogen chloride. This modified method was tested with n-butyl alcohol and found to give results like those obtained in the earlier procedure. The sealed vials were particularly advantageous where dry hydrogen chloride was added to the reaction mixture at the start.

The reversibility of the reaction was tested by dissolving equal molal quantities of ethyl *p*-nitrobenzoate and dry hydrogen chloride in anhydrous ether. The mixture was kept at 25° in the thermostat for forty-three hours. The hydrogen chloride was not absorbed, showing that the tendency to reverse must be very small under the conditions at which the reaction rates were measured. Dry hydrogen chloride was prepared by dropping pure concentrated sulfuric acid onto C. P. sodium chloride, passing the gas through two wash bottles containing pure concentrated sulfuric acid and finally through a 50-cm. column of phosphorus pentoxide.

In two trials the products of the reaction were shown to have no effect on the rate. Equal molal quantities of n-butyl alcohol, the acid chloride and dry hydrogen chloride were dissolved in anhydrous ether. The usual rate for n-butyl alcohol was observed, showing, in this case, that the decrease in the second-order constants could not be due to the influence of the hydrogen chloride evolved. A similar result was obtained for ethyl alcohol when a mole of ethyl p-nitrobenzoate was added to the reaction mixture at the start. The rate was unaffected by the presence of the ester in this instance.

Two experiments were carried out with n-butyl alcohol to test the effect on the rate of changing the concentrations of the reactants with respect to each other. If the reactions were of the second order, then the same rate would be observed whether the alcohol concentration were twice that of the acid chloride or *vice versa.* If, however, the reactions were of the third order, then the rate would be much greater in one case than in the other.[3]

It was found that the speed of the reaction was much faster when the concentration of the alcohol was twice that of the acid chloride than when the reverse relations were tried. Table II shows these differences. After ten hours 0.23 mole of the acid chloride had reacted when the concentrations were one mole of alcohol to half a mole of acid chloride. With the conditions reversed, however, only 0.16 mole of the acid chloride had reacted after ten hours

TABLE II

n-BUTYL ALCOHOL WITH *p*-NITROBENZOYL CHLORIDE IN ANHYDROUS ETHER SOLUTION

Alcohol, moles per 1000 g. of ether	1.0	0.5
Acid chloride, moles per 1000 g. of ether	0.5	1.0
Moles of chloride reacted in ten hours	0.229	0.163

Development of an Equation for Calculating the Velocity Constants for the Reaction of Alcohols with *p*-Nitrobenzoyl Chloride in Ether Solution at Infinite Dilution.—The experiments just described, showing the great influence on the speed of the reaction conditioned by changing the concentration of the alcohol, both strengthened the earlier conviction that the reaction was of the third order and suggested the notion that two

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[3] This excellent method for testing the order of a reaction was employed first by van't Hoff over forty-five years ago, "Etudes de dynamique chimique," Amsterdam, 1884. Its usefulness was emphasized by A. A. Noyes in the course of an investigation of the rate of reaction of ferric chloride with stannous chloride, Noyes, *Z. physik.* Chem., 16, 554 (1895).

molecules of alcohol might be required for each molecule of chloride used. Such a process would be in harmony with certain general views[4] concerning the mechanism of organic chemical reactions. The first step could be taken to be the addition of a molecule of alcohol to the acid chloride. The unstable complex could then react with another molecule of alcohol, splitting out the ester and hydrogen chloride and giving back a molecule of alcohol.[5]

The equation for the reaction may be symbolized as follows[6]

$$A + 2B = E + F + B$$

where A = acid chloride and B = alcohol. By using the ideas of the activity theory as applied to reaction rates,[7] and Bronsted's assumption of the critical complex,[8] an equation has been developed on the basis of this mechanism for calculating the velocity constants of these esterification reactions at infinite dilution.

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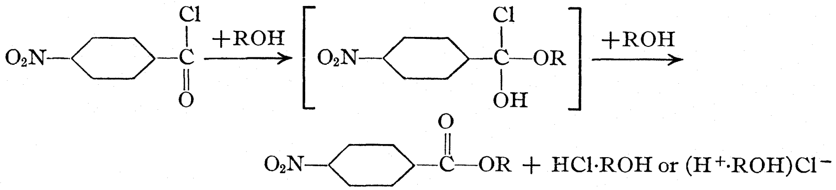
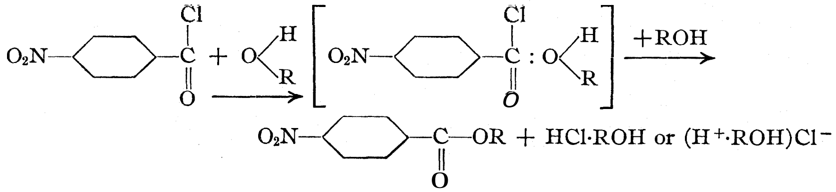
[4] See, for example, Stieglitz, *Am. Chem. J.*, **39**, *60* (1908); THIS JOURNAL, 32, 221 (1910).

[5] It is conceivable that the reaction might be formulated either on the basis of the ordinary conception of valency (a) or by making use of the electronic theory of valence (b).

(a)



(b)



Actually by rates of reaction studies, it cannot be determined whether or not the mechanism takes any one of the following courses, all of which lead to the same "complex," AB_2.

$$\begin{cases} A + B \rightleftharpoons AB \\ AB + B \rightleftharpoons (AB_2) \longrightarrow E + F + B \end{cases}$$

$$\begin{cases} B + B \rightleftharpoons B_2 \\ A + B_2 \rightleftharpoons (AB_2) \longrightarrow E + F + B \end{cases}$$

$$A + 2B \rightleftharpoons (AB_2) \longrightarrow E + F + B$$

[6] The integration of this equation and its use for chemical reactions of the third order under ideal conditions has been considered in detail by F. E. E. Germann, *J. Phys. Chem.*, 32,1748 (1928).

[7] An excellent survey of the activity theory and a bibliography have been published by Harned and Seltz, THIS JOURNAL, 44, 1475 (1922).

[8] J. N. Bronsted, *Z. physik. Chem.*, 102,169 (1922); 115,337 (1925).

According to Bronsted

$$\frac{-\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}t} = \frac{-\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}t} = KC_{\mathrm{B}}^2C_{\mathrm{A}}\frac{f_{\mathrm{B}}^2f_{\mathrm{A}}}{fx} \qquad (1)$$

where C's are concentrations, *f*'s are activity coefficients, and *fx* refers to the critical complex, AB_2. The activity theory differs from this formulation only in replacing *fx* by unity.

The alcohols give rise to very abnormal solutions, as shown by molecular weight determinations from freezing-point measurements in non-polar solvents? Unquestionably these solutions differ enough from ideality to warrant consideration. Experiments already mentioned have shown in two cases that the acid and ester formed have practically no effect on the rate of the reaction. Even greatly changing the concentration of the acid chloride does not produce a very marked influence on the rate. It appeared reasonable, therefore, to assume that the substances, other than the alcohols, did not give wide deviations from ideal solutions. Nothing could be known, of course, of the values for the critical complex, but it seemed reasonable to assume (f_{A}/fx) constant for all the solutions considered, or, in other words, that these two activity coefficients varied in the same way. This was equivalent to assuming f_{A} constant, if the activity theory be used. For simplicity it was further assumed that f_{B} depended on C_{B} only.

In accordance with the general method for dealing with rates of reactions in a changing environment, developed in the preceding paper,[10] the following equation may be written to express the realtion between the activity coefficients of the alcohols and their concentrations

$$f^2 = \frac{1}{1 - 2gC} \qquad (2)$$

where *g* is a constant dependent on the alcohol and the solvent in which it is dissolved and C is concentration expressed in moles per thousand grams of solvent.[11]

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[9] E. Beckmann, *Z. physik. Chcm.*, **2**, 638, 715 (1888); 4, 532 (1889); J. E. Eykman, *ibid.*, **2**, 964 (1888); **4**, 497 (1889); E. Paternb, *Gazz. chim. ital.*, **19**, 640 (1889); K. Auwers, Z. *physik. Chem.*, *12*, 689 (1893); Wilhelm Biltz, *ibid.*, **29**, 249 (1899); C. R. Bury and F. S. Brown, *J. Phys. Chem.*, 30,694 (1926).

[10] Scatchard, THIS JOURNAL, 52, 52 (1930).

[11] The following equations may be used to express empirically the relation between activity coefficient and concentrations. The last of the series was chosen because it leads to the fewest complications.

$$f = e^{gC}$$

$$f = 1 + gC \qquad \left\{\begin{array}{l} f = \sqrt{\dfrac{1}{1 - 2gC}} \\[2ex] f^2 = \dfrac{1}{1 - 2gC} \end{array}\right.$$

$$f = \frac{1}{1 - gC}$$

Substituting this value for f^2 in the Bronsted Equation 1 above

$$\frac{-\mathrm{d}C_B}{\mathrm{d}t} = K_3^0 \frac{C_B^2 C_A}{(1 - 2gC)} \tag{3}$$

where K_3^0 is the third-order constant at infinite dilution.

If x is the fraction of B transformed

$$C_B = C_0 (1 - x)$$
$$C_{A_0} = C_0 D,\ C_A = C_0 (D - x)$$

Substituting these values in Equation 3

$$\frac{-\mathrm{d}(C_0)(1 - x)}{\mathrm{d}t} = K_3^0 \frac{C_0^3(1 - x)^2(D - x)}{1 - 2gC_0(1 - x)} \text{ or } \tag{4}$$

$$C_0 \frac{\mathrm{d}x}{\mathrm{d}t} = K_3^0 \frac{C_0^3(1 - x)^2(D - x)}{1 - 2gC_0(1 - x)} \tag{5}$$

$$K_3^0 \mathrm{d}t = \frac{\mathrm{d}x}{C_0^2(1 - x)^2(D - x)} - 2g \frac{\mathrm{d}x}{C_0(1 - x)(D - x)} \tag{6}$$

For the case where D = 1

$$K_3^0 \mathrm{d}t = \left(\frac{1}{C_0^2} \frac{\mathrm{d}x}{(1 - x)^3}\right) - \left(\frac{2g}{C_0} \frac{\mathrm{d}x}{(1 - x)^2}\right) \tag{7}$$

Integrating, evaluating the integration constant by the condition $x = 0$, when $t = 0$, and combining terms

$$K_3^0 t = \frac{x(2 - x)}{2C_0^2(1 - x)^2} - \frac{2g}{C_0} \frac{(x)}{(1 - x)} \tag{8}$$

For the case where $D \neq 1$

$$K_3^0 \mathrm{d}t = \frac{\mathrm{d}x}{C_0^2(1 - x)^2(D - x)} - \frac{2g}{C_0} \frac{\mathrm{d}x}{(1 - x)(D - x)} \tag{9}$$

Integrating, evaluating the integration constant by the condition $x = 0$ when $t = 0$, and combining terms

$$K_3^0 t = \frac{x}{C_0^2(D - 1)(1 - x)} - \frac{1}{C_0^2(D - 1)^2} \ln \frac{D - x}{D(1 - x)} - \frac{2g}{C_0(D - 1)} \ln \frac{D - x}{D(1 - x)} \tag{10}$$

For the special case where $C_0 = 1$ and D = $^1/_2$

$$K_3^0 t = -\frac{2x}{1 - x} - 4 \ln \frac{(1 - 2x)}{(1 - x)} + 4g \ln \frac{(1 - 2x)}{(1 - x)} \tag{11}$$

Or, in terms of y, the fraction of A transformed

$$y = 2x \text{ or } x = y/2$$

$$K_3^0 t = -\frac{2y}{2 - y} - 4 \ln \frac{2(1 - y)}{2 - y} + 4g \ln \frac{2(1 - y)}{2 - y} \tag{12}$$

For the special case where $C_0 = {}^1/_2$ and D = 2

$$K_3^0 t = 4 \frac{x}{1 - x} - 4 \ln \frac{2 - x}{2(1 - x)} - 4g \ln \frac{2 - x}{2(1 - x)} \tag{13}$$

Or, in terms of y, the fraction of A transformed, $x = 2y$

$$K_3^0 t = \frac{8y}{1 - 2y} - 4 \ln \frac{(1 - y)}{(1 - 2y)} - 4g \ln \frac{(1 - y)}{(1 - 2y)} \tag{14}$$

These new equations, (7), (12) and (14), exhibit the peculiarity that the first part of each corresponds to the usual integrated form of equations for reactions of the third order. The second part is the integrated form of the equation for a second-order reaction, multiplied by the constant, *g*. In using the new equation for obtaining values of K_3^0, the constant, g, was evaluated from the data of the last observations in experiments at molal and half molal concentrations. In one case, that of n-amyl alcohol, where data on but a single run at half-molal concentration were available, using the last observation of this half-molal run led to an absurd value for g. By taking the point next to the last, the value for *g* was much more reasonable. As a check, in this case, both *g* and K_3^0 were recalculated by the method of least squares, using all thirty available observations. The value of *g* thus obtained was —0.12, against —0.13 obtained by the first method. The value for K_3^0, found in this way, was 0.106 instead of 0.108. For inactive amyl alcohol the value of g was very small, —0.01. In other words, the deviation from ideality of solutions of this alcohol in anhydrous ether apparently is very small. In all cases except *iso*-amyl alcohol the sign of the constant, g, is negative. The reason for the positive sign in this single instance is not quite clear. Considerably more study ought to be given to this alcohol.

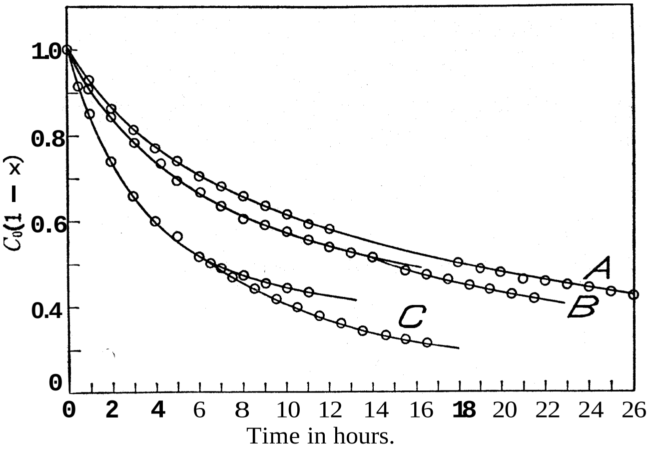

Fig. 2.—Plot of $C_0(1 - x)$ against *t* in hours for three alcohols. A, n-butyl alcohol, molal and half molal; B, ethyl alcohol, molal and half molal; C, methyl alcohol, molal and half molal.

With methyl and ethyl alcohols, the method adopted for calculating values of g gave very absurd results (—9.58 and —1.23, respectively). This circumstance led to the surmise that in these cases the hydrogen chloride evolved was producing a marked effect. Such a conclusion was borne out by the experiment showing that ethyl p-nitrobenzoate had no appreciable effect on the rate with which ethyl alcohol reacted with *p*-nitrobenzoyl chloride. This view was substantiated further by plotting the values of $C_0(1 - x)$ against t in the case of three alcohols, for molal and half-molal concentrations. For methyl alcohol the curves were markedly divergent; for ethyl alcohol the agreement was much better. With butyl alcohol, where experiment had shown the effect of added hydrogen chloride to be negligible, the curves were continuous (see Fig. 2).

If the assumption be made, in the cases of methyl and ethyl alcohols, that the effect of hydrogen chloride is equal to that attributable to the abnormality of the alcohol solutions, a reasonable value for g may be calculated by the following method.

For the third-order reaction, equal molal concentrations, the rate may be expressed by the equation

$$dx/dt = K_3^0 C_0^2 (1 - x)^3 f^2_{\mathrm{B}} \tag{15}$$

In accordance with the assumption that the effect of hydrogen chloride on the rate be equal to that of the alcohol

$$f_{\mathrm{B}}^2 = \frac{1}{1 - 2g(C_{\mathrm{B}} + C_{\mathrm{HCl}})} = \frac{1}{1 - 2gC_0} \tag{16}$$

Equation 15 may now be written

$$\frac{dx}{C_0^2(1 - x)^3} = \frac{K_3^0 dt}{(1 - 2gC_0)} \tag{17}$$

but

$$\frac{dx}{C_0^2(1 - x)^3} = K_3 dt$$

Therefore, Equation 17 may be written as follows

$$K_3 = \frac{K_3^0}{(1 - 2gC_0)} \text{ or } K_3^0 = K_3 (1 - 2gC_0) \tag{18}$$

In accordance with Equation 18 the relation between the third-order constants at molal and half-molal concentrations may be expressed in terms of g, as follows

$$K_3^1(1 - 2g) = K_3^{0.5}(1 - g) \tag{19}$$

Using the third-order constants at molal and half-molal concentrations, K_3^1 and K_3^0, the calculated values of g were -0.65 for methyl alcohol and -0.21 for ethyl alcohol. These values, in turn, gave the constants, K_3^0 0.497 and 0.144, respectively, for the two alcohols.

In the cases of five other alcohols, where data were available on experiments made with at least two different concentrations, the new equation gave results accurate within the limits of experimental error.

The deviations of the data from the equations for second- and third-order reactions and from the third-order equations for non-ideal solutions were determined by the following method. For each of the equations t was calculated, using the values of K and x or K, x and g in the case of the third-order equation for non-ideal solutions. The calculated values of t were plotted against observed values of x, on a large scale. Values of x were read off the plot at the times of observation. The differences between observed and calculated values of x were plotted against t, in hours. For *n*-butyl alcohol, to take an example, it was found that the

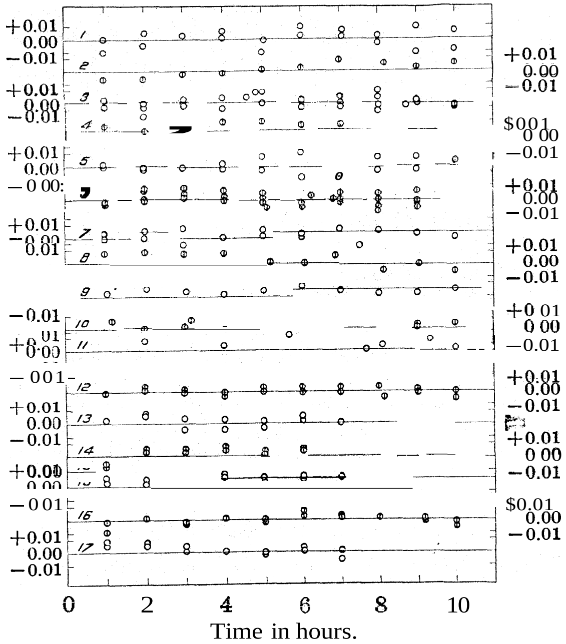

Fig. 3.—Deviations of observed values of the fraction of alcohol transformed in time, t, from the values calculated by the equation for third-order reactions. Methyl alcohol, molal (1), half molal (2); ethyl alcohol, molal (3), half molal (4); n-propyl alcohol, molal (5); n-butyl alcohol, molal (6), half molal (7), molal in alcohol, half molal in acid chloride (8), half molal in alcohol, molal in acid chloride (9); n-amyl alcohol, molal (10), half molal (11); inactive amyl alcohol, molal (12), half molal (13); iso-amyl alcohol, molal (14), half molal (15); *n*-hexyl alcohol, molal (16), half molal (17).

deviations reached as high as 7% for the second-order equation. On the other hand, they were only 2% for the third-order equation, formulated either for ideal or non-ideal solutions. Similar results were found for the other alcohols. In Fig. 3 the deviations of the observed from the calculated values of x are presented graphically. The constants obtained for the eight alcohols considered in this paper are summarized in Table III.

TABLE III

SUMMARY OF THE VELOCITY CONSTANTS FOR THE REACTION BETWEEN ALCOHOLS AND *p*-NITROBENZOYL CHLORIDE IN ANHYDROUS ETHER SOLUTION

Alcohol	K_2^1	$K_2^{0.5}$	K_3^1	$K_3^{0.5}$		g
Methyl	0.184	0.141	0.215	0.300	0.497	-0.65
Ethyl	.0853	.057	.103	.121	.144	− .21
n-Propyl	.0658	...	.0731	...	...	...
n-Butyl	.0739	.046	.0826	.0944	.118	− .25
	.0824[a]	.053[b]	.0827[a]	.1066[b]		
n-Amyl	.077	.048	.0895	.0919	.108	− .13
Inactive amyl	.035	.0195	.0373	.0386	.0387	− .01
Iso-amyl	.0695	.0325	.0751	.0668	.0571	+ .16
n-Hexyl	.0815	.053	.0940	.111	.1375	− .28

[a] Concentrations were molal in alcohol and half molal in acid chloride.

[b] Concentrations were molal in acid chloride and half molal in alcohol.

The values of these constants are averages, weighted for time. They were obtained from the ratio $\Sigma Kt/\Sigma t$. In connection with the two earlier papers, to which reference has been made,[2] it should be noted that the relative order in which the constants stand is the same, with one exception, whichever equation be used in calculating these constants. The order of n-butyl and *n*-amyl alcohols is reversed, if the third-order constants at half-molal concentration or at infinite dilution be used in making the comparison. It should be said, in all fairness, that, however, the constants for these two alcohols are calculated, they are very close together.

The writer is profoundly grateful to Professor George Scatchard of this Institute for unstinted help in developing the theoretical aspects of the problem, to Professor James F. Norris for his long-sustained interest in the work, and to many other associates at the Massachusetts Institute of Technology for significant suggestions. The data used were obtained partly by Dr. F. Cortese ("Thesis," Ph.D., Massachusetts Institute of Technology, 1926) and partly by the writer.

Summary

The reaction of alcohols with *p*-nitrobenzoyl chloride in anhydrous ether solution is of the third order, instead of the expected second order.

The mechanism of the reaction requires two molecules of the alcohol to one of the acid chloride. In other words, the reaction is second order with respect to the alcohol and first order with respect to the acid chloride.

Taking into account the well-known abnormality of alcohol solutions, an equation has been developed for calculating the third-order constants at infinite dilution,

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE MOLECULAR WEIGHTS OF AMANDIN AND OF EXCELSIN

BY THE SVEDBERG AND BERTIL SJÖGREN

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In a recent communication from this Laboratory[1] it was shown that the edestin molecule has a weight of 212,000 in a PH region from the isoelectric point *P*H 5.5 to about PH 10. At a *P*H of 11.3 definite dissociation takes place. Molecules of one-half and one-third of the normal are formed at this alkalinity. On the acid side of the isoelectric point the edestin molecule was found to be quite unstable.

Chiefly thanks to the fundamental work done by Osborne[2] a considerable number of vegetable proteins are known. Especially those which like edestin belong to the globulin group seem to be very stable and are easy to prepare in a pure state. It was thought to be of interest to study some more representatives of this important class of proteins by means of the ultracentrifuge analysis. Amandin and excelsin were first worked with because of their widely differing elementary composition. Amandin has the lowest (0.44%) and excelsin the highest (1.08%) sulfur content of the oil-seed proteins so far analyzed.

Preparation of Material

Amandin was prepared in the following way. Almonds were soaked in cold water for some hours and freed from skins. The material was then ground in a mill, and 1000 g. of the paste suspended in 5000 cc. of 10% sodium chloride solution. Toluene was added as a preservative and the mixture was digested with stirring at room temperature for twenty-four hours. After settling the solution was siphoned off and the residue treated again in the same way with 2000 cc. of 10% sodium chloride solution and after that with 1000 cc. of the same solution. By means of centrifuging the collected liquid extracts were freed from oil and fat which had been partly dissolved in the toluene. To the protein solution was then added an equal volume of saturated ammonium sulfate and some more toluene. After standing for two days at 0° the precipitate was filtered off and washed with half saturated ammonium sulfate solution. The amandin was then dissolved in a phosphate buffer 0.095 M in KH_2PO_4 and 0.005 M in Na_2HPO_4 and further containing 1% of sodium chloride in order to increase the solubility of the amandin. The solution was dialyzed against the same buffer; the final volume was 50 cc. and the concentration 2.89%.

Excelsin was isolated in the following manner. Brazil nuts were freed from the shells and ground in a mill (without removing the skins from the kernels), and 1000 g. of the paste was suspended in 5000 cc. of a 3% ammonium sulfate solution. Toluene was added as a preservative and the mixture shaken at room temperature for twenty-four hours. It was then filtered and to the solution was added ammonium sulfate to 60% saturation. The precipitate formed was dissolved in 6% ammonium sulfate, the solution was filtered and reprecipitated with ammonium sulfate to the same degree of saturation. The excelsin precipitate was washed with ammonium sulfate solution of

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[1] Svedberg and Stamm, THIS JOURNAL, 51, 2170 (1929).

[2] Osborne, "Vegetable Proteins," Longmans, Green and Co., London, 1909.

the same strength. One portion of the excelsin precipitate was dissolved in phosphate buffer of *P*H 5.5 (0.182 *M* in KH_2PO_4 and 0.018 M in Na_2HPO_4) and containing 1% ammonium sulfate and dialyzed at 0° against the same buffer. No precipitation occurred; volume of solution, 35 cc. and concentration, 3.79% (Material I). A second portion of the excelsin was dialyzed against pure water. The excelsin was precipitated in crystalline form and the crystals were dissolved as in the case of Material I: volume of solution, 50 cc.; concentration, 2.26% (Material II). The isoelectric points of these proteins are difficult to determine accurately, because of the high salt content necessary to keep them in solution. A value of *P*H 5.5–5.7 was assumed as the most probable one.[3]

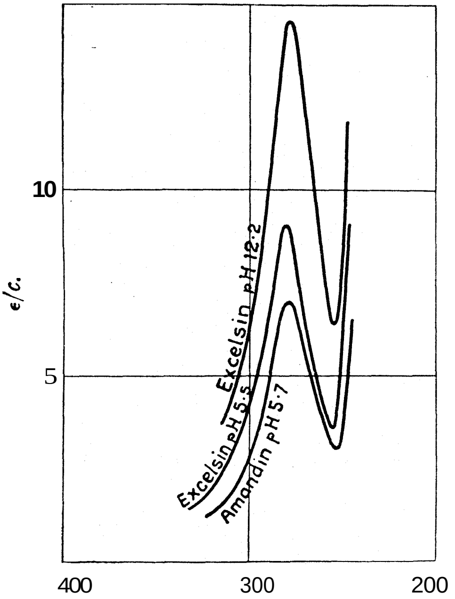

Fig. 1.

Specific Volume.—The partial specific volume was determined pycnometrically at 19.8° as described in previous communications.[4] For amandin the value 0.746 was obtained. The protein concentration was 1.4%, the solvent was 0.095 *M* in KH_2PO_4, 0.005 M in Na_2HPO_4 and contained 1% NaCl, giving a *P*H of 5.7. For excelsin the value found was 0.743. The protein concentration was 1% and the solvent was 0.182 M in KH_2PO_4, 0.018 *M* in Na_2HPO_4 and contained 1% of ammonium sulfate, giving a *P*H of 5.5.

The specific volumes for these two proteins are identical within the limits of error and also identical with the specific volumes of egg albumin, Bence–Jones protein, hemoglobin, serum albumin, serum globulin, phycocyan, phycoerythrin and edestin.

Light Absorption.—The light absorption of amandin and excelsin solutions were studied by means of the Judd–Lewis spectrophotometer. The solutions were brought to the desired concentration and *P*H directly before measuring the light absorption. Amandin was measured in 0.2 and 0.1% solutions and with a thickness of layer of 2.0 cm. The solvent was 0.095 M in KH_2PO_4 and 0.005 M in Na_2HPO_4 with 1% of NaCl, giving a *P*H of 5.5. The absorption maximum was found to be 280μμ and the minimum 253μμ. At high *P*H values where the centrifugal analysis showed that splitting up of the molecule occurs, the light absorption was found to increase.

Excelsin was measured at two different *P*H values, at 5.5 and at 12.2. In the first case two excelsin concentrations 0.10 and 0.05% made up from Material II were used in 2.0-cm. layer. The solvent was 0.182 M in KH_2PO_4 and 0.018 M in Na_2HPO_4 with 1% of ammonium sulfate. The absorption maximum was 279μμ and the minimum 253μμ. In the second case the solution was 0.06% with regard to excelsin. The solvent was 0.021 M in KH_2PO_4, 0.013 M in Na_2HPO_4, 0.030 M in NaOH and 0.12% in ammonium sulfate. The maximum was 279μμ and the minimum 253μμ. The position

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[3] Csonka, Murphy and Jones, THIS JOURNAL, 48, 763 (1926).

[4] Svedberg and Chirnoaga, *ibid.*, 50, 1401 (1928).

of the absorption band therefore is not shifted by the change in PH, but on the other hand the values of the extinction constant were much higher at the higher PH. The centrifugal analysis showed that the excelsin molecule, which at the isoelectric point is built up of six units of weight 35,000, is at a PH of 12.2 completely split up into the unit 35,000. This together with a slight formation of non-centrifugal substance accounts for the increase in light absorption at the high PH. In Fig. 1 the specific extinction coefficient, $\epsilon/c = 1/cd \times \log I_0/I$ (where c is the concentration, d the thickness of the solution, I_0 the intensity of the light beam after passing through the solvent and I the intensity after passing through the same thickness of solution), is plotted against wave length. As shown by the diagram the excelsin has a stronger light absorption than amandin. This is probably caused by the higher tryptophane content of excelsin.[5]

Determination of Molecular Weight

Sedimentation Equilibrium Method.—As shown in previous communication~ the molecular weight is given by the relation

$$M = \frac{2RT \ln (c_2/c_1)}{(1 - V\rho)\omega^2(x_2^2 - x_1^2)}$$

where R is the gas constant, T the absolute temperature, V the partial specific volume of the solute, ρ the density of solvent, w the angular velocity and c_2 and c_1 are the concentrations at the distances x_2 and x_1 from the center of rotation.

Two different types of ultracentrifuges for medium speed previously described[8,9] were used.

In Table I the result of a typical run with amandin is given and in Table II are collected the data of the five equilibrium runs made on amandin and excelsin.

TABLE I

AMANDIN. SEDIMENTATION EQUILIBRIUM RUN

Concn., 0.18%; phosphate buffer, PH 5.7 (0 095 M in KH_2PO_4, 0.015 M in Na_2HPO_4, 1% in NaCl); V = 0.746; ρ = 1.017; T = 293.2°; length of col. of soln., 0.51 cm.; thickness of col., 0.80 cm.; dist. of outer end of soln. from axis of rotation, 5.95 cm.; speed, 5350 r.p.m. (ω = 178.3~); light absorption standard, $M/300$ in K_2CrO_4; source of light, mercury lamp; light filters, chlorine and bromine; aperture of objective, F:25; plates, Imperial Process; time of exposure, 60, 120 and 180 seconds; exposures made after 38, 63 and 68 hours of centrifuging.

Distances, cm.		Mean concn., %		Number of exposures	Mol. wt.
x_2	x_1	c_2	c_1		
5.79	5.74	0 238	0.195	9	222,200
5.74	5.69	.195	.162	9	208,500
5.69	5.64	.162	.137	9	190,200
5.64	5.59	.137	.115	8	200,400
5.59	5.54	.115	.096	6	205,200
				Mean	205,300

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[5] Jones, Gersdorff and Moeller, *J. Biol. Chem.*, 62, 183 (1924).

[6] Svedberg and Fåhraeus, THIS JOURNAL, 48,430 (1926).

[7] Svedberg and Nichols, *ibid.*, 48,3081 (1926).

[8] Svedberg and Heyroth, *ibid.*, 51, 550 (1929).

[9] Svedberg and Sjögren, *ibid.*, 51,3594 (1929).

TABLE II

AMANDIN AND EXCELSIN, SUMMARY OP SEDIMENTATION EQUILIBRIUM MEASUREMENTS

Excelsin Material II was used

Solvent						
KH_2PO_4, M	Na_2HPO_4, M	1% in	PH of soln.	Concn. of protein at start, %	Mean speed, r.p.m.	Mol. wt.
0.095	0.005	NaCl	5.7	Amandin, 0.18	5,350	205,300
.095	.005	NaCl	5.7	Amandin, 0.72	4,600	210,400
.182	.018	$(NH_4)_2SO_4$	5.5	Excelsin, 0.25	4,600	213,000
.182	.018	$(NH_4)_2SO_4$	5.5	Excelsin, 0.30	4,600	212,000
.1	.1	$(NH_4)_2SO_4$	6.5	Excelsin, 0.20	4,800	210,500

As mean values for the molecular weights we find for amandin 208,000 ± 5000 and for excelsin 212,000 ± 5000.

Sedimentation Velocity Method.—For the sedimentation velocity runs the high-speed oil-turbine ultracentrifuge was used.[10] The cells were of the type described in the previous paper.[9] In most of the runs the wave length region was 290–240 μμ isolated from the mercury arc by means of chlorine and bromine filters. For the study of extremely low protein concentrations the wave length region 231–214μμ produced by means of a cadmium spark-lamp as described in the previous paper was used.[9]

In the case of amandin and excelsin the same kind of irregularities with regard to diffusion constant were observed as in the case of the Bence-Jones protein.[9] The measurement of the sedimentation constant on the other hand presented no difficulties. In the following, therefore, only a report of the latter determination will be given.

The behavior of amandin was studied within the PH region 4.3–12.2. Excelsin was investigated from PH 5.5 to PH 11.9. The solutions were

TABLE III

AMANDIN, SUMMARY OP SEDIMENTATION VELOCITY MEASUREMENTS

Speed, about 25,000 r.p.m. in the five first runs and about 42,000 r.p.m. in the last two runs

Solvent						
HAc, M	NaAc, M		NaCl, %	PH of soln.	Concn. of protein, %	$s_{20}° \times 10^{13}$
0.016	0.004		2.5	4.27	0.10	11.4[11]
KH_2PO_4, M	Na_2HPO_4, M	NaOH, M				
0.095	0.005	..	1	5.7	.18	11.3
.095	.005	..	1	5.7	.50	11.2
.095	.005	..	1	5.7	1.45	12.1
.050	.050	..	1	7.05	0.29	11.3
.006	.032	0.002	0.07	9.40	.20	11.2
.003	.013	.031	.03	12.16	.10	[a]

[a] Decomposition, 59% of molecules of 208,000 and 41% of 34,500.

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[10] Svedberg and Nichols, THIS JOURNAL, 49, 2920 (1927); Svedberg, "Colloid Chemistry," 2d ed., The Chemical Catalog Co., Inc., New York, 1928, p. 153.

[11] The directly measured value, 11.1×10^{-13}, was corrected for the increased density and viscosity of the solvent due to the high salt content in the same way as described by Svedberg and Stamm, Ref. 1.

brought to the desired concentration and *PH* immediately before starting a run. In Table III are summarized the determinations on amandin, in Table IV the determinations on excelsin.

TABLE IV

EXCELSIN, SUMMARY OF SEDIMENTATION VELOCITY MEASUREMENTS

Material I was used for Runs 2–5, Material II for Runs 1 and 6–10

No.	Solvent KH_2PO_4, M	Na_2HPO_4, *M*	$(NH_4)_2SO_4$, %	*PH* of soln.	Concn. of protein, %	Speed. r.p.m.	Obs.	s_{20}° X 10^{13} Corr.
1	0.182	0.018	1	6.5	0.03[a]	25,600	10.3	11.4
2	.182	.018	1	5.5	.12	24,800	10.6	11.8
3	.182	.018	1	5.5	.20	24,300	10.7	11.8
4	.182	.018	1	5.5	.76	23,400	11.1	12.4
5	.182	.018	1	5.5	1.03	44,900	10.5	11.7
6	.182	.018	1	5.5	1.13	23,500	10.9	12.1
7	.1	.1	1	6.47	0.32	24,500	10.9	12.2
8	.013	.187	0.13	7.46	.13	23,400	..	11.3
9[b]	.022	.030	.12	9.81	.11	40,900	..	11.3
10[c]	.021	.013	.12	11.88	.11	....	..	3.54

[a] Cadmium light was used. [b] 0.005 M in sodium hydroxide. [c] 0.040 M in sodium hydroxide.

As shown by Table III amandin is stable within the *PH* range 4.3–9.4. The mean value of the sedimentation constant is 11.4 X 10^{-13}. A non-centrifugible substance was not present in the solutions studied. In Fig. 2 a diagram of the microphotometer curves from the run at PH 12.16 is given. The diagram shows that at this PH the solution contains two different centrifugible substances (together with a small amount of a non-centrifugible substance). In Fig. 3 the last curve corresponding to the state of the solution after two hours of centrifuging is given after being reduced to represent relative concentrations (Curve D) instead of merely galvanometer deflections as in Fig. 2. In the same diagram are given (in dotted lines) the curves for the undecomposed amandin (A), for a protein of molecular weight one-sixth of the normal amandin (B) and for a mixture of 59% normal amandin and 41% of amandin of weight one-sixth of the normal substance (C). The closeness of the two curves C and D makes it very probable that the normal amandin at a *PH* of 12.16 is to a large extent split up into molecules of one-sixth of

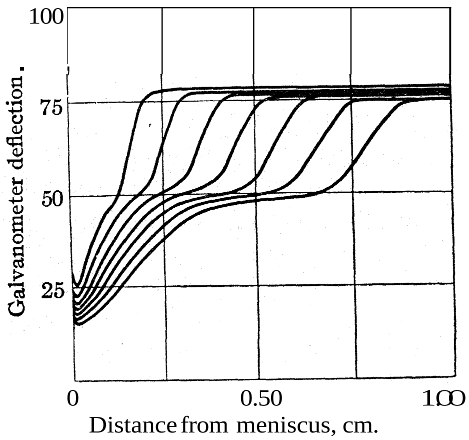

Fig. 2.

the normal weight. Because of the difficulty of taking into account the difference in light absorption between the normal and the decomposed amandin, the calculation of the relative amounts of the two components in the mixture should be regarded only as a first approximation.

Table IV shows that excelsin is stable within the PH range 5.5–9.81, with *a* mean corrected sedimentation constant of 11.8×10^{-13}. A small amount of a non-centrifugible substance was present. At a PH of 11.88 the protein was completely broken up into a substance possessing a sedimentation constant of 3.54×10^{-13}. Now this is, within the limit of error, the same value as that found for egg albumin (**3.32** $\times 10^{-13}$) and for Bence-Jones protein (3.55×10^{-13}), which have been shown to have a molecular weight of one-sixth of that of normal excelsin. It is therefore extremely probable that in the solution of *P*H 11.88 the excelsin is broken up into molecules of one-sixth the weight of normal excelsin.

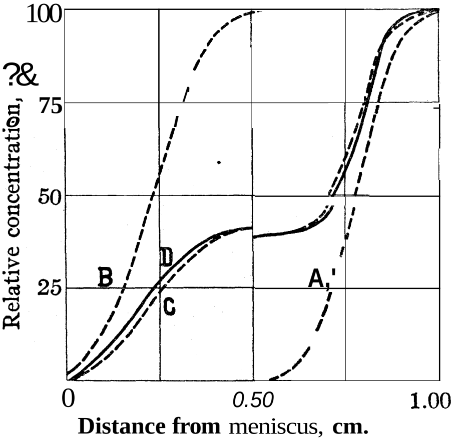

Fig. 3.

A test of the reversibility of the disaggregation of the excelsin molecule was performed. A solution identical with the one used for Run 10 (of PH 11.88) which had been shown to possess a sedimentation constant of 3.54×10^{-13}, indicating a molecular weight of one-sixth of normal excelsin, was dialyzed for seven days against a phosphate buffer of PH 6.5 (0.1 M in KH_2PO_4, 0.1 M in Na_2HPO_4 and 1% in ammonium sulfate). As shown by Table IV, excelsin has its normal molecular weight at the PH of 6.5. During the dialysis a small amount of insoluble substance appeared and was filtered off. The determination of the sedimentation constant gave 11.7×10^{-13} (corrected value). A small amount of non-centrifugible substance was present and also traces of a centrifugible substance of lower sedimentation constant. The light absorption had very nearly assumed the value corresponding to undecomposed excelsin (compare Fig. 1). The disaggregation of the excelsin molecule into molecules one-sixth of **normal** excelsin is therefore practically reversible.

Discussion of Results

The sedimentation equilibrium measurements have shown that amandin has a molecular weight of 208,000 ± 5000 and excelsin a weight of 212,000 ± 5000 near their isoelectric points. These values are, within the limits of error, identical with those previously found for edestin,[1] R-phycoerythrin,[12,13] R-phycocyan and C-phycocyan[13] near their isoelectric points. At higher PH values the molecules of all these proteins have been found to break up into simple sub-multiples of the isoelectric molecule. With regard to PH stability R-phycoerythrin resembles amandin inasmuch as at a PH of 11.0 its molecules are to an amount of about 25% disaggregated into molecules of the weight one-sixth of that of the normal molecule. The sedimentation velocity measurements have shown that at a PH of 12.2 the amandin molecule is to an extent of about 41% disaggregated into molecules of weight one-sixth of the normal.

Excelsin seems to be somewhat less stable than amandin. Its PH stability region is smaller and it shows a tendency to form a non-centrifugible decomposition product, which is not the case with amandin.

The values of the sedimentation constants 11.41×10^{-13} for normal amandin and 11.78×10^{-13} for normal excelsin are within the limits of error identical with the values found for the proteins just mentioned in the vicinity of their isoelectric points. A calculation of the molar frictional constants f at 20° by means of the formula, $f = [M(1 - V\rho)]/s$, gives for amandin 4.63×10^{16} and for excelsin 4.63×10^{16}, while the values of f_s to be expected for spherical molecules of the same weight and specific volume, calculated by means of the formula $f_s = 6\pi\eta N(3MV/4\pi N)^{1/3}$, are for amandin 4.50×10^{16} and for excelsin 4.52×10^{16}. The ratio f/f_s, which for a spherical molecule should be unity, is for amandin 1.03 and for excelsin 1.02. The radius of the molecule, derived from the formula $r = (3MV/4\pi N)^{1/3}$, is for amandin 3.94 $\mu\mu$ and for excelsin 3.96 $\mu\mu$.

It seems to be of interest to be able to compare the values for the frictional constant and the radii of edestin, R-phycoerythrin, R-phycocyan, and C-phycocyan with the values for amandin and excelsin. Those other values have therefore been calculated. In order to give a more complete review of the data of the six proteins with molecular weights near 208,000, Table V has been arranged so as to contain molecular weight, M, sedimentation constant, s, molar frictional constant, f, molar frictional constant for a spherical molecule, f_s, dissymmetry ratio f/f_s and radius r.

TABLE V

COLLECTED VALUES

Protein	Molecular weight	$s \times 10^{13}$	$f \times 10^{-16}$	$f_s \times 10^{-16}$	f/f_s	r, $\mu\mu$
Amandin	208,000 = 6.04 × 34,500	11.4	4.63	4.50	1.03	3.94
Excelsin	212,000 = 6.15 × 34,500	11.8	4.63	4.52	1.02	3.96
Edestin	208,000 = 6.04 × 34,500	12.8	4.16	4.50	0.93	3.94
R-Phycoerythrin	209,000 = 6.06 × 34,500	11.5	4.61	4.51	1.02	3.95
R-Phycocyan	206,000 = 5.97 × 34,500	11.1	4.51	4.51	1.00	3.95
C-Phycocyan	208,000 = 6.04 × 34,500	11.2	4.74	4.50	1.05	3.94

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[12] Svedberg and Lewis, THIS JOURNAL, 50, 525 (1928).

[13] Svedberg and Katsurai, *ibid.*, 51, 3573 (1929).

Within the limit of error all the corresponding data of Table V are equal for the six proteins in question.[14] Thus it is obvious that the mass and the shape of the molecules of these proteins are almost identical. The six proteins in question have different chemical composition, different isoelectric points and different light absorption. Their P_H stability ranges are also different but the molecular weights of the products of alkaline disaggregation are simple sub-multiples of the normal molecule. So far only the sub-multiples $^1/_2$, $^1/_3$, $^1/_6$ have been observed. It is very remarkable that these sub-multiples are identical with the normal molecular weights of other proteins. Thus all the 12 native and stable proteins so far investigated in this Laboratory as well as their disaggregation products—with the possible exception of the hemocyanins, which have molecular weights of the order of millions—can all as a first approximation be derived from the unit 34,500 by multiplying with the integers *two,* three and *six.*

The expenses connected with these experiments have been defrayed by grants from the foundation "Therese och Johan Anderssons Minne" and from the Nobel Fund of Chemistry.

Summary

1. The molecular weights and P_H stability regions of amandin and excelsin have been studied by means of the ultracentrifugal methods.

2. Amandin is stable from P_H 4.3 to about 10 with a molecular weight of 208,000 ± 5000. At a P_H of 12.2 it is partly disaggregated, forming molecules with a weight one-sixth of the normal ones. The sedimentation constant is 11.41×10^{-13} and the molar frictional constant 4.63×10^{16} for the normal molecules. The molecules of normal amandin are spherical with a radius of 3.94 $\mu\mu$.

3. Excelsin is stable from P_H 5.5 to about 10, possessing a molecular weight of 212,000 ± 5000. At a P_H of 11.9 excelsin is completely disaggregated into molecules of one-sixth of the molecular weight of normal excelsin. The sedimentation constant is 11.78×10^{-13} and the molar frictional constant 4.63×10^{16} for the normal molecules. The sedimentation constant is 3.54×10^{-13} for the disaggregated molecules. The aggregation and disaggregation processes are reversible. The normal excelsin molecules are spherical with a radius of 3.96 $\mu\mu$.

4. The molecular weight, sedimentation constant, molar frictional constant and molecular radius of amandin and excelsin have been compared with the corresponding constants of edestin, R-phycoerythrin, R-phycocyan and C-phycocyan and have been found to be identical within the limits of error.

5. The disaggregation products of these six proteins have been found

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[14] The sedimentation constant for edestin and the other data containing this constant are uncertain because of the high salt content of the solution.

to belong to one or more than one of the sub-multiples $^1/_2$, $^1/_3$ or $^1/_6$ of the normal molecule. The molecular weights of these sub-multiples correspond to normal molecular weights of other proteins.

UPSALA, SWEDEN

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

CYCLIC QUATERNARY AMMONIUM SALTS FROM HALOGENATED ALIPHATIC TERTIARY AMINES

BY E. R. LITTMANN AND C. S. MARVEL

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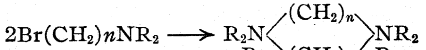
The formation of rings from open-chain compounds of various types has been the subject of many recent investigations. The work of Ruzicka[1] and his collaborators on the large carbon rings has led to this study of the nitrogen compounds in the hope of obtaining large rings containing a nitrogen atom in place of one of the carbon atoms. The largest simple ring containing a nitrogen atom heretofore described is the seven-membered ring, hexamethylene-imine, which has recently been characterized by Müller and Sauerwald.[2]

In a recent study of bromo tertiary amines[3] it was observed that 4-bromobutyldiethylamine on standing changed into a quaternary ammonium salt, which was thought to be a pyrrolidine derivative. The ease with which this reaction occurred suggested that other brominated tertiary amines might give the desired larger rings containing nitrogen.

Knorr and Roth[4] have studied bromo-ethyldimethylamine and chloropropyldimethylamine and have found that they reacted to give six- and eight-membered rings containing two nitrogen atoms, according to the general reaction



$$2Br(CH_2)_nNR_2 \longrightarrow \underset{Br}{R_2N}\langle\begin{smallmatrix}(CH_2)_n\\(CH_2)_n\end{smallmatrix}\rangle\underset{Br}{NR_2}$$

Von Braun and his students[5] have studied bromo-alkyl primary amines of the type $Br(CH_2)_nNH_2$ and have found that when $n = 4$, 5 or 6 some of the cyclic nitrogen compound was obtained, although the yields were low and by-products due to secondary reactions formed the greater part of the final product. When $n = 7$, they were unable to obtain a reaction product that could be identified as the cyclic amine. In addition to these

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[1] The fourteenth paper on large carbocyclic rings by Ruzicka and his co-workers was published in *Helv. Chim. Acta*, 11, 1174 (1928).

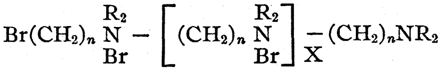
[2] Muller and Sauerwald, *Monatsh.*, 48, 527, 731 (1927).

[3] Marvel, Zartman and Bluthardt, THIS JOURNAL, 49, 2299 (1927).

[4] Knorr and Roth, *Ber.*, 39, 1425 (1906).

[5] Von Braun and Steindorff, *ibid.*, 38, 173, 3089 (1905); Von Braun and Müller, *ibid.*, 39, 4116 (1906); Von Braun and Beschke, *ibid.*, 39, 4121 (1906).

two types of reactions, bromo-alkylamines of this general type might be expected to unite to form long-chain molecules of the type



$$Br(CH_2)_n\overset{R_2}{\underset{Br}{N}} - \left[(CH_2)_n\overset{R_2}{\underset{Br}{N}}\right]_X - (CH_2)_nNR_2$$

According to the views recently expressed by Carothers,[6] ring formation would be the main reaction to be expected when n has the value 4 or 5. When n has a value greater than 5, the reaction would be expected to give the long open-chain polymeric type of compound.

The present paper describes the preparation and reactions of bromoamines of the general type $Br(CH_2)_nN(CH_3)_2$, where n has a value of 4, 5, 6 and 7. All of these amines react with themselves to give cyclic quaternary ammonium salts to a greater or less degree. Where n has the value 4, 5 or 6, ring formation proceeds as the major reaction and yields of more than 50% of the cyclic salt have been isolated. When n has the value 7, the yield of cyclic compound is lowered to less than 50% but still represents a fairly large amount of the final product. These results are shown in Table I, where they are compared with the yields of the cyclic ketones which Ruzicka[7] has obtained by the distillation of the salts of dibasic acids.

TABLE I

COMPARISON OF THE YIELDS OF CYCLIC KETONES AND CYCLIC QUATERNARY AMMONIUM SALTS

Ketone	Yield, %	Quaternary ammonium salt	Yield, %
$(CH_2)_4{>}CO$	45	$(CH_2)_4{>}N(CH_3)_2Br$	76
$(CH_2)_5{>}CO$	70	$(CH_2)_5{>}N(CH_3)_2Br$	63
$(CH_2)_6{>}CO$	50	$(CH_2)_6{>}N(CH_3)_2Br$	56
$(CH_2)_7{>}CO$	20	$(CH_2)_7{>}N(CH_3)_2Br$	37

That the products isolated in this work were really rings was determined by comparing the five- and six-membered rings with known pyrrolidine and piperidine derivatives. The seven-membered ring was found to be identical with the corresponding derivative of Müller and Sauerwald's[2] hexamethylene-imine. The molecular weights of these salts were determined by freezing point depression in water. They showed the behavior of typical uni-univalent salts in that the values obtained were slightly over one-half the calculated value. No eight-membered ring containing nitrogen was available for comparison with the compound which was obtained from bromoheptyldimethylamine. However, its molecular weight from freezing point depression data checks with the value expected for the simple cyclic salt.

Attempts to determine the rate of the ring closing reaction quantitatively

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[6] Carothers, THIS JOURNAL, 51, 2548 (1929).

[7] The figures in the table are the highest reported in the paper of Ruzicka, Brugger, Pfeiffer, Schinz and Stoll, *Helv. Chim. Acta*, 9, 505 (1926).

by titration of ionic halogen and thus make it possible to compare the ease of formation of rings of different sizes were not successful. The side reactions proceeded to a sufficient extent to invalidate reaction rate studies,

Experimental Part

4-Phenoxybutyldimethylamine.—To 180 cc. of a solution of dimethylamine (0.2 g. of amine per cc.) in absolute alcohol was added 46 g. of 4-phenoxybutyl bromide. The solution was allowed to stand overnight and then heated on a steam-bath for about one-half hour. The alcohol and excess dimethylamine were removed by distillation, the residue was treated with a 25% aqueous solution of sodium hydroxide and the amine was extracted with ether. The ether was evaporated and the amine was distilled under reduced pressure. The yield was 30 g. (77% of the theoretical amount) of a product, b. p. 122–124" (5 mm.); sp. gr. $^{20}_{20}$ 0.951; n^{20}_{D} 1.5017. This compound has previously been described by von Braun,[8] who prepared it by the distillation of 5-phenoxybutyltrimethylammonium hydroxide. The chloroplatinate was prepared and recrystallized from dilute alcohol; m. p. 104".

Anal. Subs., 0.1382: Pt, 0.0338. Calcd. for $(C_{12}H_{19}ON)_2 \cdot H_2PtCl_6$: Pt, 24.52. Found: Pt, 24.45.

5-Phenoxyamyldimethylamine.—A solution of 163 g. of 5-phenoxyvaleric acid in 250 cc. of absolute alcohol containing 10 cc. of concentrated sulfuric acid was refluxed for about five hours. The ester was isolated in the usual way. The yield was 169 g. (90% of the theoretical amount) of ethyl 5-phenoxyvalerate; b. p. 151° (6 mm.); sp. gr. $^{20}_{20}$ 1.041; n^{20}_{D} 1.4982.

Anal. Subs., 0.2130: CO_2, 0.5025; H_2O, 0.1557. Calcd. for $C_{13}H_{18}O_3$: C, 64.48; H, 8.11. Found: C, 64.39; H, 8.10.

This ester was reduced to 5-phenoxyamyl alcohol by the method described by Marvel and Tanenbaum[9] for the preparation of 4-phenoxybutyl alcohol. From 110 g. of ester, 110 g. of sodium and 1 liter of absolute alcohol there was obtained 45 g. (50% of the theoretical amount) of 5-phenoxyamyl alcohol; b. p. 152–155° (5 mm.); m. p. 36°. This compound was previously described by von Braun, Deutsch and Schmatloch,[10] who prepared it by the action of oxygen on 5-phenoxyamylmagnesium iodide.

5-Phenoxyamyl bromide was prepared by mixing 55 g. of phosphorus tribromide and 90 g. of the alcohol at 0° and gradually allowing the mixture to come to room temperature. Water was added to the mixture and the product was separated and distilled. The yield was 63 g. (52% of the theoretical amount) of product; b. p. 154–155° (5 mm.); sp. gr. $^{20}_{20}$ 1.199; n^{20}_{D} 1.5240. Von Braun and Steindorff[11] have previously prepared this compound from sodium phenolate and pentamethylene bromide.

5-Phenoxyamyldimethylamine was prepared from 25 g. of the bromide and 18 g. of dimethylamine in alcohol solution. The yield was 15.5 g. (74% of the theoretical amount) of a product, b. p. 132–134° (5 mm.); sp. gr. $^{20}_{20}$ 0.945; n^{20}_{D} 1.4997. Von Braun[12] has previously prepared this amine by the distillation of 5-phenoxyamyltrimethylammonium hydroxide. The chloroplatinate was prepared. After crystallization from dilute alcohol it melted at 112°.

Anal. Subs., 0.2032: Pt, 0.0481. Calcd. for $(C_{13}H_{21}ON)_2 \cdot H_2PtCl_6$: Pt, 23.69. Found: Pt, 23.70.

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[8] Von Braun, *Ann.*, **382**, 35 (1911); von Braun and Deutsch, *Ber.*, 44,3701 (1911).

[9] Marvel and Tanenbaum, THIS JOURNAL, 44,2648 (1922).

[10] Von Braun, Deutsch and Schmatloch, *Ber.*, 45, 1250 (1912).

[11] Von Braun and Steindorff, *ibid.*, 38,963 (1905).

[12] Von Braun, *Ann.*, **382**, 36 (1911).

6-Phenoxyhexyldimethylamine.—Ethyl 6-phenoxycaproate was prepared by esterifying with ethyl alcohol the crude 6-phenoxycaproic acid obtained from 147 g. of diethyl 4-phenoxybutylmalonate. The yield was 75 g. (63% of the theoretical amount) of a product, b. p. 157–159° (3 mm.); sp. gr. $^{20}_{20}$ 1.031; n^{20}_{D} 1.4928.

Anal. Subs., 0.2103: CO_2, 0.5461; H_2O, 0.1592. Calcd. for $C_{14}H_{20}O_3$: C, 71.18; H, 8.46. Found: 70.86; H, 8.41.

By reduction of 70 g. of this ester with sodium and absolute alcohol, there was obtained 32 g. (55% of the theoretical amount) of 6-phenoxyhexyl alcohol; b. p. 152–154° (3 mm.); m. p, 31°. Von Eraun, Deutsch and Schmatloch[10] have previously prepared this alcohol by the action of oxygen on 6-phenoxyhexylmagnesium bromide.

6-Phenoxyhexyl bromide was prepared by the action of 18 g. of phosphorus tribromide on 30 g. of the alcohol. The yield was 23 g. (54% of the theoretical amount) of a product; b. p. 155–156° (3 mm.); sp. gr. $^{20}_{20}$ 1.248; n^{20}_{D} 1.5361.

Anal. Subs., 0.2376: 16.3 cc. of 0.0549 *N* $AgNO_3$. Calcd. for $C_{12}H_{17}OBr$: Br, 31.1. Found: Br, 30.8.

6-Phenoxyhexyldimethylamine was prepared from 22 g. of the bromide and 60 cc. of a 33% alcoholic dimethylamine solution. The yield was 14 g. (74% of the theoretical amount) of a product, b. p. 132–134° (3 mm.); sp. gr. $^{20}_{20}$ 0.942; n^{20}_{D} 1.4988.

The chloroplatinate was prepared and after recrystallization from dilute alcohol melted at 126°.

Anal. Subs., 0.1920: Pt, 0.0438. Calcd. for $(C_{14}H_{23}ON)_2 \cdot H_2PtCl_6$: Pt, 22.91. Found: Pt, 22.86.

7-Phenoxyheptyldimethylamine.—Diethyl 5-phenoxyamylmalonate was prepared from 81 g. of 5-phenoxyamyl bromide. The yield was 67 g. (63% of the theoretical amount) of a product, b. p. 202–204° (4–5 mm.); sp. gr. $^{20}_{20}$ 1.508; n^{20}_{D} 1.4882. The ester was impure and contained some unchanged bromide. It was not purified further but was used directly to give 7-phenoxyheptoic acid.

The crude malonic ester (65 g.) was saponified with boiling aqueous potassium hydroxide solution and the mixture was acidified. The malonic acid was separated and heated to drive out carbon dioxide. The crude 7-phenoxyheptoic acid thus obtained was esterified with ethyl alcohol. The yield was 31.5 g. (61% of the theoretical amount) of ethyl 7-phenoxyheptoate; b. p. 161–163° (3 mm.); sp. gr. $^{20}_{20}$ 1.015; n^{20}_{D} 1.4932.

Anal. Subs., 0.1345: CO_2, 0.3524; H_2O, 0.1066. Calcd. for $C_{15}H_{22}O_3$: C, 72.00; H, 8.80. Found: C, 71.48; H, 8.87.

Reduction of 30 g. of this ester with sodium and absolute alcohol gave 16 g. (60% of the theoretical amount) of phenoxyheptyl alcohol; b. p. 157–158° (3 mm.); m. p. 34°.

Anal. Subs., 0.2545: CO_2, 0.6985; H_2O, 0.2214. Calcd. for $C_{13}H_{20}O_2$: C, 75.00; H, 9.62. Found: C, 74.81; H, 9.68.

The bromide was prepared by treating 13 g. of the alcohol with 13 g. of phosphorus tribromide. The yield was 13.5 g. (80% of the theoretical amount) of a product, b. p. 154–157° (3 mm.); sp. gr. $^{20}_{20}$ 1.199; n^{20}_{D} 1.5240.

Anal. Subs., 0.1421: AgBr, 0.0981. Calcd. for $C_{13}H_{19}OBr$: Br, 29.52. Found: Br, 29.39.

7-Phenoxyheptyldimethylamine was obtained by treating 15 g. of the bromide with 4 cc. of 30% alcoholic dimethylamine solution. The yield was 12 g. (82% of the theoretical amount) of a product, b. p. 158–160° (8 mm.); sp. gr. $^{20}_{20}$ 0.939; n^{20}_{D} 1.4980.

The chloroplatinate was prepared and after recrystallization from dilute alcohol melted at 162°.

Anal. Subs.. 0.2029: Pt, 0.0446. Calcd. for $(C_{16}H_{25}ON)_2 \cdot H_2PtCl_6$: Pt, 22.20. Found: Pt, 22 00.

ω-Bromo-alkyl Dimethylamines.—The bromo-amines were prepared from the corresponding phenoxy derivatives by the action of hot 48% hydrobromic acid. The general procedure was to prepare a solution of 20 g. of the phenoxyamine in 100 cc. of 48% hydrobromic acid. This solution was distilled until the temperature of the vapors reached 123–125°. Then a second 100-cc. portion of 48% acid was added and the distillation was continued until the total distillate amounted to about 175 cc. This operation was carried out in all-glass apparatus to avoid contamination from the stoppers.

The residue in the distilling flask was evaporated to dryness under reduced pressure on a steam-bath. The crude bromo-amine hydrobromide was dissolved in about 30–35 cc. of water and the free amine was liberated by the addition of a 28% solution of sodium hydroxide. The solution was cooled in an ice-bath during the decomposition of the salt with the alkali. The amine was collected in ether and the ether then removed by evaporation under reduced pressure. If possible the amine was distilled under reduced pressure.

4-Bromobutyldimethylamine.—This amine was never definitely isolated due to too rapid formation of cyclic quaternary salt. Attempts were made at −10° and in a carbon dioxide–ether bath but no pure product could be obtained.

5-Bromo-amyldimethylamine.—This amine was obtained in ether solution at low temperatures, but attempts at distillation always resulted in the formation of the quaternary salt. The ether solution was extracted with dilute hydrochloric acid and the acid solution treated with an excess of gold chloride. The crystalline chloro-aurate was recrystallized from dilute alcohol and then melted at 57°.

Anal. Subs., 0.1943: Au, 0.0715. Calcd. for $C_7H_{16}NBr \cdot HAuCl_4$: Au, 36.95. Found: Au, 36.75.

6-Bromohexyldimethylamine.—This amine was distilled under reduced pressure without the formation of very large quantities of cyclic quaternary salt. It boiled at 78–80" (6 mm.). Attempts to determine the density and index of refraction gave very poor results since enough salt formed during the work to prevent any degree of accuracy. The chloro-aurate of some freshly distilled amine was prepared and crystallized from dilute alcohol. It melted at 111°.

Anal. Subs., 0.1199: Au, 0.0423. Calcd. for $C_8H_{18}NBr \cdot HAuCl_4$: Au, 35.98. Found: Au, 35.52.

7-Bromoheptyldimethylamine.—This amine was distilled under reduced pressure. Very little material was lost due to salt formation during the distillation. It boiled at 85–87° (7 mm.); sp. gr. $^{20}_{20}$ 1.029; n^{20}_{D} 1.4695. The chloro-aurate was prepared and after crystallization from dilute alcohol it melted at 126°.

Anal. Subs., 0.1021: Au, 0.0361. Calcd. for $C_9H_{20}NBr \cdot HAuCl_4$: Au, 35.10. Found: Au, 34.96.

Cyclic Quaternary Ammonium Salts

N-Dimethylpyrrolidinium Bromide.—Upon the addition of an excess of strong sodium hydroxide solution to 30–35 cc. of a solution of 4-bromobutyldimethylamine hydrobromide in water, prepared as described for the preparation of the bromo-amines from the corresponding phenoxy derivatives, the quaternary salt was precipitated as a crystalline mass. After filtration the product was crystallized from a mixture of 80% ethyl acetate and 20% absolute alcohol. There was obtained 13–14 g. of product (72–76% of the theoretical amount). The salt did not melt below 325° (uncorr.).

Anal. Subs., 0.0870: 8.36 cc. of 0.0549 N $AgNO_3$. Calcd. for $C_6H_{14}NBr$: Br. 43.5. Found: Br, 43.7.

The molecular weight of the N-dimethylpyrrolidinium bromide was determined cryoscopically. Subs., 0.6922: H_2O, 24.905; At, 0.556°. Calcd. for $C_6H_{14}NBr$: mol. wt., 180. Found: mol. wt., 92.6. A further check on the identity of this compound was made by converting it to the chloro-aurate of N-dimethylpyrrolidinium chloride, previously described by Willstatter and Huebner.[13]

Approximately 1 g. of the dimethylpyrrolidinium bromide was treated with an excess of an aqueous suspension of silver oxide. After shaking for one to two hours, all of the halogen was removed from the aqueous solution and the mixture filtered. The filtrate was then acidified with hydrochloric acid and to this solution was added an excess of gold chloride. The chloro-aurate so prepared melted at 282° (uncorr.) after recrystallization from water. Willstätter and Huebner have recorded the melting point as 286° (uncorr.), with decomposition. A second sample of the chloro-aurate showed no depression upon taking a mixed melting point with the chloro-aurate prepared from N-dimethylpyrrolidinium chloride which in turn had been prepared from pure pyrrolidine by the following method. Two to three g. of pyrrolidine was treated with an excess of methyl iodide in the presence of an excess of aqueous 20% sodium hydroxide solution. The insoluble N-dimethylpyrrolidinium iodide was removed by filtration, treated with an excess of an aqueous suspension of silver oxide, and converted to the chloro-aurate with hydrochloric acid and gold chloride as described above.

N-Dimethylpiperidinium Bromide.—This salt was obtained in two ways. A portion of a solution of 5-bromo-amyldimethylamine in alcohol was evaporated and the product purified by crystallization. The same product was obtained when an ether solution of the bromo-amine was evaporated and the residue allowed to solidify at room temperature. The crude salt was recrystallized from a mixture of 50% ethyl acetate and 50% absolute alcohol. The pure salt melted at 324° (uncorr.).

Anal. Subs., 0.1110: 10.14 cc. of 0.0549 N $AgNO_3$. Calcd. for $C_7H_{16}NBr$: Br, 41.3. Found: Br, 41.2. The molecular weight was determined cryoscopically. Subs., 0.6166; H_2O, 24.904; At, 0.448°. Calcd. for $C_7H_{16}NBr$: Mol. wt., 194. Found: mol. wt., 100.

The structure of the N-dimethylpiperidinium bromide was confirmed by converting it to the chloroplatinate of N-dimethylpiperidinium chloride, which has been described by von Braun[14] as melting at 209–210°. The bromide was converted to the chloride as described under the pyrrolidinium salts. The chloroplatinate was prepared by the addition of chloroplatinic acid to the aqueous solution of dimethylpiperidinium chloride. It melted at 243° (uncorr.), with decomposition, after crystallization from water. Since this melting point did not agree with the one recorded by von Braun, a sample of the piperidine derivative was made for comparison.

Approximately 5 g. of piperidine was converted to N-dimethylpiperidinium chloride by the method used for the corresponding pyrrolidinium derivative. The aqueous, acid solution so obtained was treated with an excess of chloroplatinic acid and the salt crystallized from water. The chloroplatinate melted at 241° (uncorr.).

Anal. Subs., 0.1219: Pt, 0.0371. Calcd. for $(C_7H_{16}N)_2 \cdot PtCl_6$: Pt, 30.6. Found: Pt, 30.4.

Since pure 5-bromo-amyldimethylamine could not be isolated except in ether, the amount of ring compound formed was determined on a sample of amine which had been allowed to stand in alcohol for two months. About 5 cc. of bromo-amyldimethylamine hydrobromide solution which was equivalent to approximately 3 g. of bromo-amine was neutralized and extracted with ether as indicated in the general method. The

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[13] Willstatter and Heubner, *Ber.*, 40, 3873 (1907).

[14] Von Braun, *ibid.*, 33, 2735 (1900).

ether solution was transferred to a flask containing about 50 cc. of alcohol and the mixture allowed to stand. The quantity of bromo-amine lost during the neutralization as quaternary salt was not determined, although it was considerable. After standing the solvent was evaporated from the bromo-amine solution and the residue (0.65 *g.)* separated by fractional crystallization. The crude product thus obtained was dissolved in the minimum quantity of boiling solvent, composed of equal parts of ethyl acetate and absolute alcohol, and the solution cooled. After filtration, the filtrate was concentrated to incipient crystallization and again cooled. This process was repeated until the fractions became too small to handle, when the soluble end was mixed with all the previously used filter papers, extracted with alcohol, evaporated to dryness and the mixture again crystallized from the ethyl acetate–alcohol mixture. From the 0.65 g. of crude product there were obtained 0.413 *g.* of pure dimethylpiperidinium bromide and 0.23 g. of material that was slightly less pure.

N-Dimethylhexamethylene-iminium Bromide.—In one experiment a portion of the solution of 6-bromohexyldimethylamine in alcohol was evaporated and in another the pure distilled amine was allowed to solidify in the absence of a solvent. In either case the same product was obtained. Without a solvent the formation of quaternary salt seemed to take place more rapidly. The crude salt was crystallized from absolute alcohol, after which it melted at 289° (uncorr.).

Anal. Subs., 0.0940: 7.81 cc. of 0.0549 N $AgNO_3$. Calcd. for $C_8H_{18}NBr$: Br, 38.45. Found: Br, 38.70.

The molecular weight of N-dimethylhexamethylene-iminium bromide was determined cryoscopically. Subs., 0.2873: H_2O, 24.904; *At,* 0.165°. Calcd. for $C_8H_{18}NBr$: mol. wt., 208. Found: mol. wt., 130.

The structure of the N-dimethylhexamethylene-iminium bromide was determined by converting to a known derivative. Müller and Sauerwald[2] prepared the corresponding iodide and found it to melt at 265° (corr.).

About 1 *g.* of the dimethylhexamethylene-iminium bromide was shaken with an excess of an aqueous supension of silver oxide for one to two hours. After filtration the filtrate was acidified with hydriodic acid and evaporated to dryness. After crystallization from absolute alcohol the iodide thus obtained melted at 255° (uncorr.).

A sample of distilled 6-bromoheuyldimethylamine was allowed to stand at room temperature until the mass solidified. The product was then dissolved in the minimum quantity of boiling solvent composed of 80% ethyl acetate and 20% absolute alcohol. The fractionation was carried out in the same way as for the corresponding piperidine derivative. From 10 *g.* of the distilled amine there was obtained 5.6 *g.* of the pure quaternary ammonium salt.

N-Dimethylheptamethylene-iminium Bromide.—This salt could be obtained in appreciable quantity only by reaction of the bromo-amine with itself in the absence of a solvent. The formation of quaternary ammonium salt in alcohol was so slow that practically no material could be isolated during a reaction period of several weeks. A sample of distilled 7-bromoheptyldimethylamine was allowed to stand overnight. The solid mixture which formed was crystallized from the minimum quantity of a mixture of equal parts of ethyl acetate and absolute alcohol. The pure N-dimethylheptamethylene-iminium bromide melted at 268° (uncorr.).

Anal. Subs., 0.1326: AgBr, 0.1114. Calcd. for $C_9H_{20}NBr$: Br, 36.02. Found: Br, 35.86.

The molecular weight of N-dimethylheptamethylene-iminium bromide was determined cryoscopically. Subs., 0.2433: H_2O, 24.890; *At,* 0.165°. Calcd. for $C_9H_{20}NBr$: mol. wt., 222. Found: mol. wt., 111.

A second sample of bromo-amine was allowed to solidify overnight and the ring compound separated by crystallization from the above ethyl acetate–alcohol mixture in the same way as the dimethylpiperidinium bromide. There was thus obtained 0.59 g. of pure quaternary ammonium salt from 1.57 g. of the amine.

Summary

1. Halogenated aliphatic tertiary amines of the type $Br(CH_2)_nN(CH_3)_2$, in which n has the values 4, 5, 6 and 7 have been prepared.

2. These amines react with themselves to form cyclic quaternary ammonium salts in yields which indicate that ring formation is the principal reaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE MECHANISM OF CARBOHYDRATE OXIDATION. XI. THE ACTION OF POTASSIUM HYDROXIDE ON MALTOSE

BY WILLIAM LLOYD EVANS AND MARJORIE PICKARD BENOY

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The fact that maltose is a disaccharide makes a study of its behavior toward aqueous solutions of potassium hydroxide a much more complex problem than is the case with the monosaccharides for the reason that it may react in any one or all of three general ways. (a) The molecule of maltose may undergo hydrolysis[1] into two molecules of glucose. In this case one should expect the experimental data obtained from equivalent solutions of glucose and maltose to be quantitatively the same. (b) Since maltose is a reducing sugar like glucose, there exists the possibility of the disaccharide molecule undergoing enolization[2] and subsequent decomposition without hydrolysis having taken place previously. (c) It is evident that both reactions may take place simultaneously, the extent to which the maltose is changed in either direction being probably dependent on such experimental factors as alkali concentration and temperature. To obtain data with reference to the behavior of maltose in alkaline solutions, when examined from this general standpoint, was the first objective of these experiments.

If maltose is found to react in accordance with possibility (b) or (c), the mechanism of the alkaline decomposition of the disaccharide might depend upon the presence of an equilibrated mixture of six glucosido-hexoses, maltose and its isomers, analogs of the sugars in the well-known de Bruyn and van Ekenstein systems. These would be maltose (4-glucosido-d-glucose), 4-glucosido-d-mannose, 4-glucosido-*d*-fructose, 4-glucosido-pseudo-*d*-fructose, 4-glucosido-d-a-glutose and 4-glucosido-*d*-β-glutose.[3] Under the

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[1] Lewis and Buckborough, THIS JOURNAL, 36, 2385 (1914).

[2] Nef, Ann., 403, 381 (1914).

[3] Nef, *ibid.*, 403, 382 (1914).

conditions employed in our experiments, these glucosido sugars should react to give a series of 4-glucosido-hexose enediols. It is conceivable that these maltose isomers together with the 4-glucosido-hexose enediols and also the hexose sugars arising from any possible hydrolysis of the 4-hexosido-hexose sugars might form in these reaction mixtures a more general equilibrated condition which could be influenced by such experimental factors as the alkali concentration and the temperature.[4] To obtain some experimental data with reference to this latter point of view was the second objective of this study.

Experimental Part

The general procedures used in these experiments were exactly the same as those described in previous reports[5] from this Laboratory concerning the action of aqueous solutions of potassium hydroxide on the trioses and certain hexoses.

Materials. (a) Carbohydrates.—Maltose-monohydrate, d-glucose and *d*-mannose were purchased on the market and were found to be of the highest degree of purity.

(b) Reagents.—All reagents used in the various experimental operations were examined by the usual laboratory procedures as to their fitness for this study.

Manipulations. (a) Maltose and Potassium Hydroxide.—A 0.25 molar solution of maltose monohydrate was made by dissolving 2.251 g. of the disaccharide in 25 cc. of potassium hydroxide solution of the desired normality. This was agitated for forty-eight hours in a thermostat at the desired temperature. During this time the flask was kept closed with a well-fitting rubber stopper. At the end of the reaction period the solution was worked up for formic, acetic and lactic acids.

(b) Analytical Methods.—The necessary qualitative and quantitative methods have been described previously.

(c) Determination of Mannose Phenylhydrazone.—A portion of mannose weighing 2.251 g. was dissolved in a mixture of 25 cc. of potassium hydroxide solution of such strength as to give the final desired normality, 17.5 cc. of 95% alcohol and 5 cc. of phenylhydrazine. After this reaction mixture had been agitated in a thermostat at 25° for two hours, a light-colored precipitate was observed to separate out. At the end of forty-eight hours the solid was filtered, washed with acetone to remove any pyruvic aldehyde osazone, dried *in vacuo* at 55° and then weighed. The product was of a pale buff color. Samples were also similarly prepared using an equivalent weight of *d*-glucose. These were arranged into two groups: (1) the first group consisted of samples all of the same alkalinity (0.105 N), which were used as a time run, specimens being removed at intervals of several days, filtered, washed and weighed; (b) the second group of samples of varying alkali normalities was removed from the thermostat at the end of fourteen days, filtered, washed with acetone, dried and weighed. An exactly similar procedure was carried out with maltose, the time being twenty-six days.

The material was identified as mannose hydrazone by the known solubility of the compound in various reagents and by a comparison of its

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[4] Cf. Evans, Edgar and Hoff, THIS JOURNAL, 48, 2666 (1926).

[5] (a) Evans, Edgar and Hoff, *ibid.*, 48, 2665 (1926); (b) Evans and Hass, *ibid.*, 48, 2703 (1926); (c) Evans and Cornthwaite, *ibid.*, 50, 486 (1928); (d) Evans and Hutchman, *ibid.*, 50, 1496 (1928); (e) Evans and O'Donnell, *ibid.*, 50, 2543 (1928); (f) Evans, ***Chem. Reviews,*** 6, 281 (1929).

melting point with that of mannose hydrazone prepared from pure d-mannose in cold acetic acid solution. Our results on the latter method of identification are the following.

Mannose hydrazone from glucose	178–180°
Mannose hydrazone from mannose	178–180°
Mixture of the above two	182°
Mannose hydrazone from mannose	181°
Mixture of mannose hydrazone from both mannose and maltose	192°
Mannose hydrazone from mannose	190°

The brackets indicate that the samples were heated simultaneously. Because of the known variation in melting points of hydrazones and osazones with a change in the rate of heating, all such determinations recorded in our experiments were made by direct comparison with known material. The agreement between these two was considered much more significant than that with values recorded in the literature.[6] The melting point of mannose hydrazone recorded by Reiss, Tollens and Gans[7] is 186–188°, and that by Fischer is 196–200°.

The effect of varying the rate of heating is clearly shown in the following test carried out on some pure mannose-hydrazone used as a standard of comparison.

Rate of heating, degrees/minute	4	7	8
Melting point, °C.	178–180	183–186	190

The mannose hydrazone was a pale cream color when first precipitated, a pale buff after one crystallization from water and a decided yellow after a second crystallization. The color deepened to an orange if the material was allowed to stand overnight in contact with water. It came out of alcohol solution much lighter in color. Corrections were made for the solubility of the mannose phenylhydrazone in the data given in Fig. 6.

(d) **Pyruvic** Aldehyde.—Pyruvic aldehyde was determined as an osazone by the general method described by Evans and Hass.[5b]

Experimental Results.—The quantitative data obtained from our reaction mixtures are shown in graphical form in Figs. 1–6.

Theoretical Part

In attempting to outline the decomposition mechanism of maltose in alkaline solutions, one is confronted with an appalling lack of knowledge with reference to the possible complex reaction products. More particularly, the difficulties in dealing with the experimental data obtained from the action of aqueous solutions of potassium hydroxide on maltose lie in the following facts: (a) the five theoretically possible 4-glucosido-hexoses,

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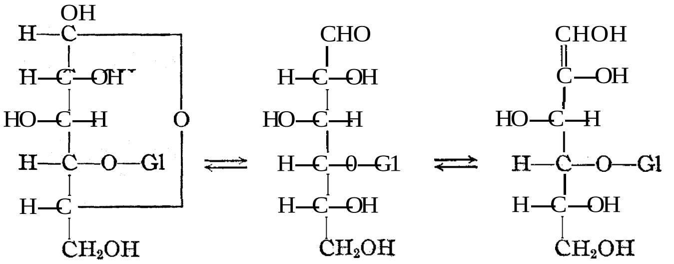
[6] Fischer, Ber., 21, 987 (1888); 22, 1156 (1889).

[7] Reiss, Tollens and Gans, *ibid.*, 22,610 (1889).

isomers of maltose, are unknown; (b) there is also much work to be done in the development of sharp methods for the quantitative separation of many known organic products which are obtained by the action of alkalies on the sugars. The recently established proof[8] that maltose is 4-glucosido-d-glucose increases the complexity of the problem. Maltose can no longer be regarded as glucose with an inactive glucosido section attached in such a way as not to interfere with the activity of the glucose portion of the molecule. The attachment at the fourth carbon atom makes a vital difference because it limits the extent of the enediolization. The yields of pyruvic aldehyde osazone, mannose hydrazone, lactic and acetic acids obtained by the interaction of maltose and potassium hydroxide at 25 and 50° are smaller than those obtained from equivalent solutions of glucose under exactly the same experimental conditions, while those of formic acid are greater. An[8a] examination of these facts seems to show that their quantitative aspects are best understood on the assumption that maltose, in alkaline solution, reacts to form a series of 4-glucosido-glucose enediols which may rupture at the double bond. The products obtained by such a fission may then react with the alkali present much after the well-known behavior of the hexose sugars under similar experimental conditions.

The following explanation is offered to account for the relative yields of reaction products found in our experiments on the alkaline decomposition of maltose when compared to those from glucose.

(a) Maltose-1,2-enediol (4-Glucosido-glucose-1,2-enediol).—The formation of maltose-1,2-enediol may be shown by the following equation



(1)

Maltose Maltose, aldehydo form[a] Maltose-1,2-enediol
Gl = Glucosido

A rupture of the maltose-1,2-enediol **(4-glucosido-glucose-1,2-enediol)** would result in the formation of 3-glucosido-arabinose and hydroxymethylene, as is shown in the reaction

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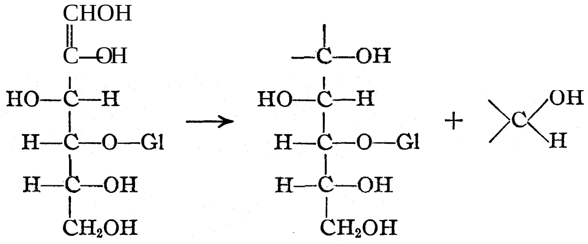
[8] Irvine and Black, *J. Chem. Soc.*, 129, 862–875 (1926); Cooper, Haworth and Peat, *ibid.*, 129, 876 (1926); Levene and Sobotka, *J. Biol. Chem.*, **71**, 471–475 (1927); Zemplén, *Ber.*, **60B**, 1555–1564 (1927).

[8a] Cf. K. Bernhauer, *Biochem. Z.*, **210**, **175**, 1929.

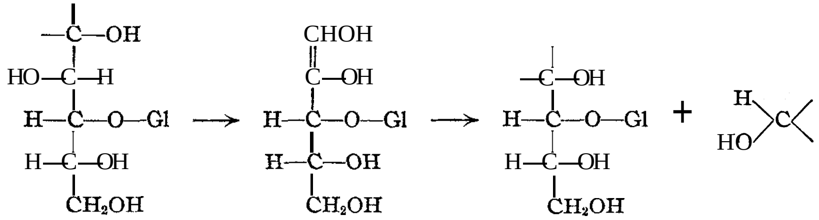
[9] Wolfrom, This Journal, 51, 2188 (1929).



Maltose-1,2-enediol 3-Glucosido-arabinose, active form Hydroxy-methylene (2)

If sufficiently mild oxidizing agents were present, it is clear that 3-glucosido-arabonic and formic acids would be the reaction products. In the presence of potassium hydroxide maltose is oxidized by potassium permanganate to oxalic acid and carbon dioxide together with traces of acetic acid. The general relationship of the quantities of reaction products to the alkali concentration in the oxidation is in general similar to that of glucose.[10]

The 3-glucosido-arabinose thus formed may then in turn undergo an enediol formation with subsequent splitting into hydroxymethylene and 2-glucosido-erythrose. This change is shown in the equation



3-Glucosido-arabinose, active form 3-Glucosido-arabinose-1,2-enediol 2-Glucosido-erythrose, active form Hydroxy-methylene (3)

Under appropriate oxidizing conditions 2-glucosido-erythronic acid should be formed at this point. In connection with the possible formation of the 3-glucosido-arabinose and 2-glucosido-erythrose, it is of much interest to point out that Glattfeld and Hanke[11] oxidized maltose in an alkaline solution with air and with hydrogen peroxide. When the glucosido acids which they obtained as reaction products were hydrolyzed, they identified erythronic acid lactone and arabonic acid, the latter being recognized by means of its phenylhydrazide.

If the enediol formation can proceed no further, *i. e.*, if the CHO-Gl group remains intact, then it is possible for the 2-glucosido-erythrose to undergo hydrolysis with the formation of erythrose and glucose. This change is shown in the equation

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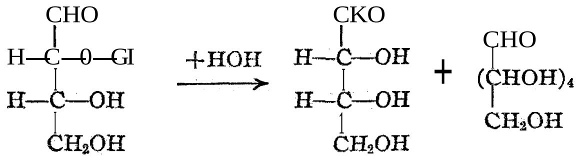
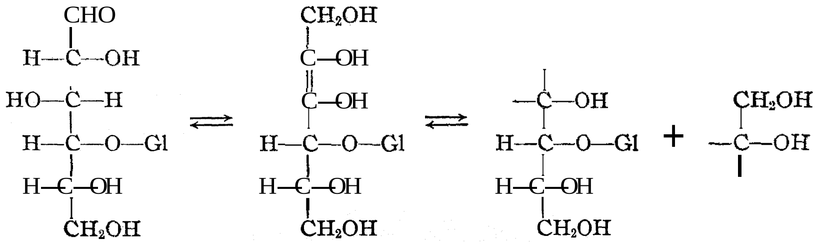
[10] Unpublished results.

[11] Glattfeld and Hanke, THIS JOURNAL, 40, 992 (1918).



2-Glucosidoerythrose Erythrose Glucose (4)

(b) **Maltose-2,3-enediol (4-Glucosido-glucose-2,3-enediol).**—As the temperature of the reaction and the concentration of the alkali are increased, there should be mote of a tendency for the general equilibrated condition present in the maltose solution to shift in the direction of forming a maltose-2,3-enediol, *i. e.*, **4-glucosido-glucose-2,3-enediol.** Its behavior in this respect would be represented by the reaction



Maltose, aldehydo form Maltose-2,3-enediol 2-Glucosido-erythrose, active form Glycol-aldehyde, active form (5)

Then it is clear that the 2-glucosido-erythrose thus formed would also yield glucose and erythrose as shown in Equation 4. If the mechanism of the alkaline decomposition of maltose is correctly set forth in these equations, then it is possible to offer a satisfying explanation for the relative amounts of lactic, acetic and formic acids and pyruvic aldehyde when this disaccharide is treated with aqueous solutions of potassium hydroxide under the same conditions of alkali normality and temperature as the monosaccharide, glucose.

Lactic Acid.—From the above-outlined decomposition of the maltose molecule it is seen that one molecule of the disaccharide may yield the following general results: (a) two molecules of hydroxymethylene, one molecule of erythrose and one molecule of glucose (Equations 1, 2, 3 and 4); (b) or it may yield one molecule of glycol aldehyde, one molecule of erythrose and one molecule of glucose (Equations 5 and 4). From a study of these possibilities it may be shown that only one-half of the maltose molecule yields lactic acid and that that portion of the disaccharide molecule is the glucosido section.[11a]

It has been established recently that the yields of lactic acid obtained from alkaline solutions of glucose are a function of both the alkali concentration and the temperature of the reacting system. An examination of

[11a] *Cf.* H. Wolff, *Biochem. Z.*, 210, 459 (1929).

Fig. 1 will show that the general characteristics of lactic acid formation in alkaline solutions of maltose are also practically the same as those obtained from glucose except that the yield is less in the case of the disaccharide, *i. e.*, it tends to be somewhat less than one-half at both temperatures.

Nef reached the conclusion that the tetroses in alkaline solutions did not give rise to the formation of a 1,2-enediol, *i. e.*, $CH_2OHCHOHC(OH)=CHOH$. The formation of this enediol would be essential because on fission it would yield glyceric aldehyde, a necessary intermediate in the production of lactic acid in alkaline solutions of the sugars. It is quite possible that the speed of rearrangement of the 1,2-enediol to the corresponding saccharinic acid is too rapid when compared to that of glyceric aldehyde formation. Nef came to his point of view because he found that *glycol aldehyde*[12] *did not yield the least trace of lactic acid* **when** it was *treated with S N potassium hydroxide solution.* However, he did obtain significant amounts of four carbon atom saccharinic acid (1,3-dihydroxybutyric acid), a fact which shows that a tetrose sugar had formed under the conditions of his experiments.[13] These general findings were confirmed in this Laboratory, although alkaline solutions were employed of lesser normality than those used by Nef.

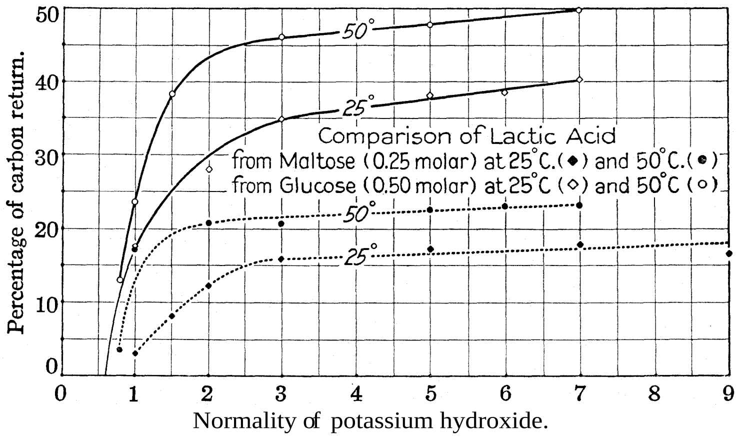


Fig. 1.

By reason of the facts pointed out in the two preceding paragraphs, namely, that glucose in alkaline solution will yield lactic acid and that erythrose under the same conditions will not do so, it is clear that on the basis of the above-outlined decomposition of maltose the conclusion must be reached that the source of the lactic acid in this reaction is the glucosido section of the disaccharide molecule and not the glucose section.

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[12] Nef, *Ann.*, 376, 40 (1910).

[13] *Cf.* Fischer and Landsteiner, *Ber.*, 25,2553 (1892).

Since 0.25 molar maltose (equivalent to 0.50 molar glucose) and 0.50 molar glucose solutions were used, it is now evident that the lactic acid yields from maltose should tend to be one-half those which could be obtained from glucose. On the basis that the lactose molecule is 4-galactosido-glucose, it may be predicted safely that this well-known sugar will not yield much lactic acid when treated with aqueous solutions of potassium hydroxide under the same conditions that were used in our maltose study. This arises from the fact that the hexosido section of the milk sugar molecule[3] does not give rise to much lactic acid in alkaline solutions, while the hesose seticon of this sugar gives rise to a tetrose which, as is pointed out above, does not give the 1,2-enediol which is necessary for lactic acid formation. Mr. Robert C. Hockett of this Laboratory is at present studying the behavior of the disaccharides toward aqueous solutions of potassium hydroxide.

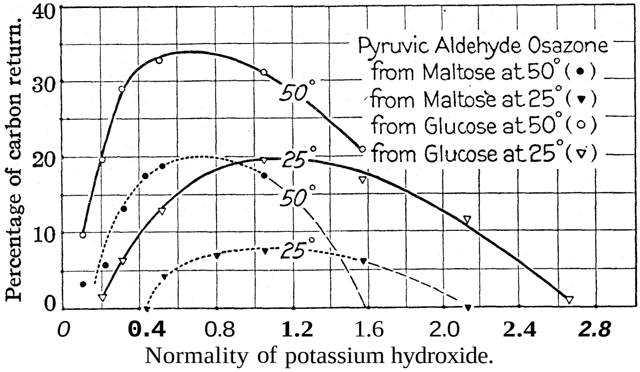

Fig. 2.

Should 3-glucosido-arabinose hydrolyze to any great degree, the yields of lactic acid should tend to be greater than those which we found, because Mr. Rollin F. Conaway of this Laboratory has shown recently that arabinose in alkaline solutions will yield pyruvic aldehyde, which changes under these conditions to lactic acid.

Pyruvic Aldehyde Osazone.—If the above reactions of maltose take place, then the disaccharide in alkaline solution should give rise to yields of pyruvic aldehyde osazone in amounts which approximate one-half those obtained from equivalent solutions of glucose. By our experimental methods this was shown in general to be true (Fig. 2). Pyruvic aldehyde is the forerunner of lactic acid. It is derived from the glyceric aldehyde obtained through a splitting of the 3,4-enediol of the glucosido section of the maltose molecule. Alkaline solutions of glycol aldehyde do not give rise to pyruvic aldehyde osazone when the experiment is carried out under the same conditions as are used with sugars that do so react. Hence, any tetrose formed from glycol aldehyde will not give a 1,2-enediol, a reaction necessary for the production of glyceric aldehyde, which, in turn, is the forerunner of pyruvic aldehyde.

Formic Acid.—It has been pointed out previously that formic acid may arise from the action of alkalies on hydroxymethylene. In the above equations it is seen that the glucose section of the maltose molecule yields at least two molecules of hydroxymethylene. Since erythrose forms a 2,3-enediol in preference to a 1,2-enediol, then two molecules of glycol aldehyde (active form) will form according to the equation

$$\mathrm{CH_2OHC(OH){=}C(OH)CH_2OH \rightleftharpoons 2CH_2OH\overset{\diagdown\diagup}{C}(OH)} \qquad (6)$$

It has been shown in this Laboratory that alkaline solutions of glycol aldehyde will yield formic acid. Since the glucosido section of the maltose molecule will yield formic acid also, then it becomes clear from all of these facts that alkaline solutions of maltose should produce more formic acid than do equivalent alkaline solutions of glucose. From the data in Fig. 3 this comparison is found to be true.

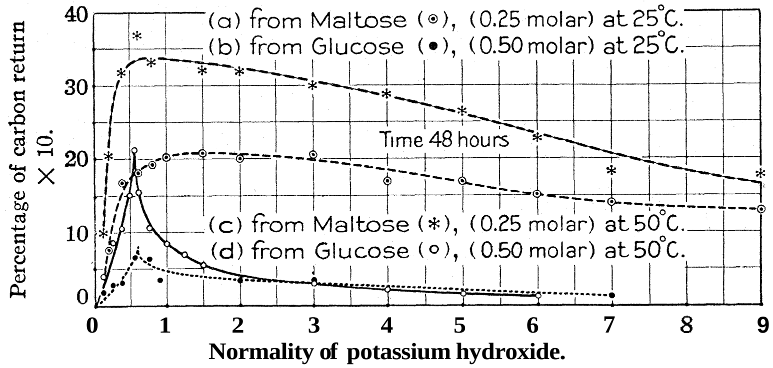

Fig. 3.—Comparison of formic acid.

Acetic Acid.—Our data, Fig. 4, with reference to acetic acid production in alkaline solutions of maltose show that this acid is found in smaller amounts than it is in alkaline solutions of glucose. The possible sources of acetic acid arising from the alkaline decomposition of maltose as given by the above equations may be these: (a) pyruvic aldehyde formed in the alkaline decomposition of the glucosido section of the maltose molecule; (b) the glycol aldehyde obtained in Equation 5 and also that arising from the splitting of the tetrose-2,3-enediol in Equations 4 and 5. Since not over 1% of glycol aldehyde carbon is returned as acetic acid under the conditions of these experiments, then from our data it may be fairly concluded that the principal source of acetic acid in these maltose reactions must be the glucosido section of the disaccharide molecule. From these statements it is clear that the amounts of acetic acid obtained from maltose must be less than those arising from equivalent solutions of glucose. Whether 2,3-dihydroxybutyric acid formed from the action of potassium hydroxide on the tetrose present will yield acetic acid has not yet been established.

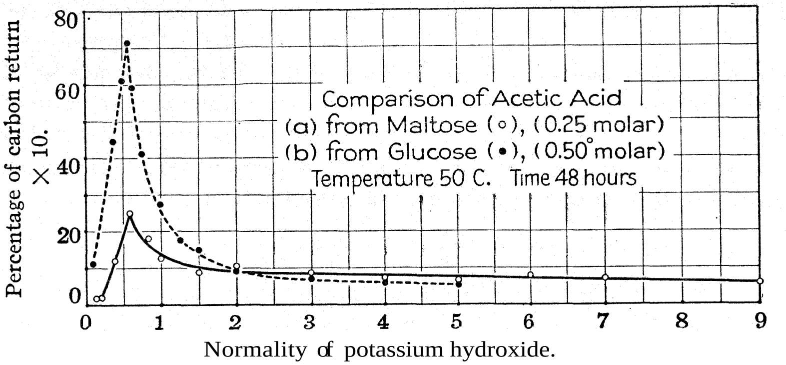

Fig. 4.

Production Relation of Reaction Products.—From Fig. 5 it is seen that the data obtained for pyruvic aldehyde osazone, lactic, acetic and formic acids from alkaline solutions of maltose are of the same general character as those which have been obtained previously in this Laboratory from glucose, mannose and fructose, a fact which would seem to support the points of view set forth in the above explanation of the mechanism involved in the alkaline decomposition of maltose.

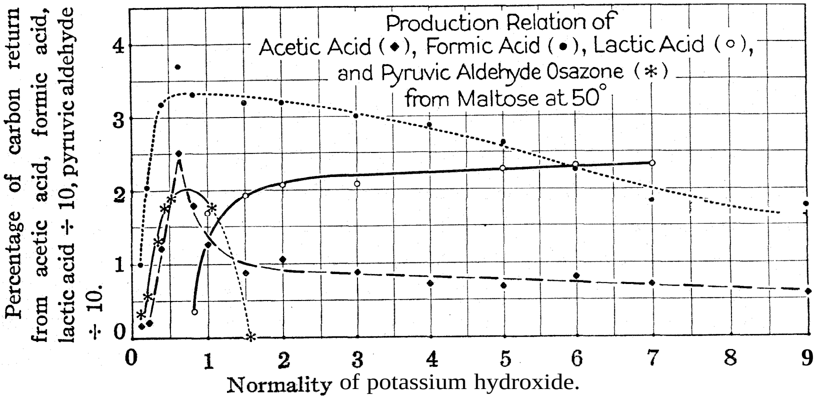

Fig. 5.

Effect of Temperature and Alkali Concentration.—Our data on the alkaline decomposition of maltose show that the effects of alkali concentration and increased temperature are of the same general type as those obtained with the hexose sugars.

The Hydrolysis of Maltose. (a) **Mannose Hydrazone.**—De Bruyn and van Ekenstein[14] obtained d-mannose phenylhydrazone from maltose after boiling it for three hours in a **0.166** N potassium hydroxide solution. Kolb[15] also obtained it at room temperature after the sugar had stood with a dilute barium hydroxide solution for a long period. It is clear that the mannose in these two cases might have arisen from the following sources. (1) Glucose arising from the possible hydrolysis of maltose would be converted into the well-known series of hexose sugars, one of which is mannose. (2) The theoretically possible 4-glucosido-mannose might be hydrolyzed into its possible monosaccharide units. The possibility of the existence of the 4-glucosido-mannose in an alkaline solution seems to be borne out by the fact that Lewis[16] obtained mannonic acid lactone from the hydrolysis of the glucosido products resulting from the oxidation of maltose with alkaline copper hydroxide. To *obtain mannose as its hydrazone from an alkaline solution of maltose would therefore seem to be proof that an hydrolysis of a 4-glucosido-hexose compound had occurred.* The results of our experiments are shown in Fig. **6.** The first formation of a noticeable precipitate of mannose phenylhydrazonefrom maltose in **0.105** N potassium hydroxide solution occurred after eleven days at 25°. A corresponding sample of d-glucose under similar conditions showed some precipitate in five days, thus making it appear that the conversion of maltose into its monosaccharide

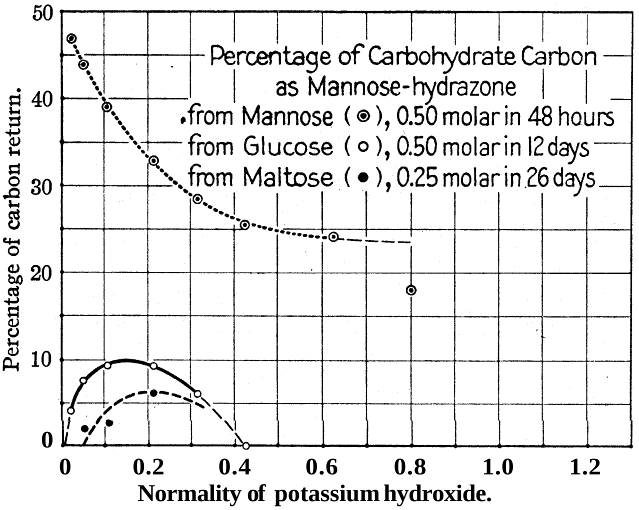

Fig. 6.

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[14] Lobry de Bruyn and Alberda van Ekenstein, *Rec. trav. chim.*, *18*, 147–149 (1899); *cf.* 15, 92 (1896).

[15] Kolb, *Biochem. Z.*, *63*, 1–57 (1914).

[16] Lewis, *Am. Chem. J.*, 42, 301–314 (1909).

units by either Mechanism 1 or 2 required about the same length of time as the formation of the mannose phenylhydrazone from glucose. The formation of the hydrazone directly from mannose is very rapid since precipitation began within two hours. In the long periods during which these sugars were exposed to the action of alkaline solutions, longer for maltose than for d-glucose, the mannose hydrazone was no doubt being decomposed, so that sharp comparisons between the curves cannot be made nor far-reaching conclusions drawn, but some interesting suggestions are contained in the data. (1) A comparison of corresponding points on the two curves shows that the maltose values are approaching those for d-glucose, and also that the hydrolysis of maltose or its glucosido isomers is a function of the alkalinity.[17] (2) The rise in the two curves shows that the de Bruyn and van Ekenstein equilibrium is disturbed by changes in the alkali normality. (3) The downward trend of these curves is thought to be due to the fact that the hexose enediols are beginning to undergo splitting at their double bonds, a reaction which would result in lowering the available concentration of the hexose sugars. It is a noteworthy fact in this connection that the maxima are between 0.15–0.20 N alkali, a value slightly above that (0.05 N) which Nef[18] indicated as the point where enediolic splitting first begins for the hexoses. The only significance of the mannose curve is that it marks off the regional limits in which we might hope to find the hydrazone in the case of the other sugars. This curve is taken as a measure of the decrease in the concentration of the aldehydo form of this sugar in the presence of an increase in the alkali normality. This seems to be in harmony with the point of view expressed by Wohl and Neuberg[19] and Fischer with reference to the non-formation of the hydrazones from the salts of the enediols.

(b) Pyruvic Aldehyde **Osazone.**—A comparison of the mannose phenylhydrazone curves from maltose and glucose with those of pyruvic aldehyde osazone obtained from these sugars seems to indicate very strongly that an increase in the concentration of the alkali causes a change in the equilibrium present which favors a splitting of the maltose enediols. Such *a* change should result in a decrease in the yields of derivatives obtained from 4-glucosido-hexose sugars and an increase in the products arising from the fission of glucosido sugars containing less than 12 carbon atoms. Attention is directed to the fact that the mannose hydrazone formation from both glucose and maltose ceases at approximately the same alkalinity (0.42 N) as that at which pyruvic aldehyde formation begins at 25°.

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[17] Nef, Ann., 403, 207 (1914).

[18] Nef, *ibid.*, 403, 206 (1914).

[19] Wohl and Neuberg, Ber., 33, 3099 (1900); Fischer, *ibid.*, 28, 1149 (1895); cf., Zemplén and Kunz, *ibid.*, 56, 1705 (1923).

Summary

1. Objectives of these experiments were as follows: (a) to determine whether maltose in alkaline solutions reacts in accordance with the views that postulate the presence of hexosido-hexose-enediols or whether it undergoes hydrolysis at the glucosido union; (b) to ascertain whether temperature and the concentration of the alkali used influence the character of the reaction products.

2. (a) Maltose was dissolved in aqueous solutions of potassium hydroxide of various normalities (0.1–9.0), the sugar concentration being 0.25 molar. After forty-eight hours of agitation at 25 and 50°, the reaction mixtures were quantitatively examined for acetic, lactic and formic acid. (b) Similar aqueous-alcoholic solutions of maltose, phenylhydrazine and potassium hydroxide were examined for pyruvic aldehyde osazone.

3. Maltose yields larger amounts of formic acid than glucose does under exactly the same conditions, while smaller amounts of pyruvic aldehyde osazone, lactic and acetic acids are obtained than from the hexose sugar.

4. These quantitative differences between maltose and glucose have been explained on the assumption that the disaccharide forms two enediols, namely, maltose-1,2-enediol (4-glucosido-glucose-1,2-enediol) and maltose-2,3-enediol (4-glucosido-glucose-2,3-enediol)). Since the glucosido linkage is on the fourth carbon atom, it is further assumed that the 4-glucosido-glucose-3,4-enediol does not rupture, if formed.

5. Maltose-1,2-enediol (4-glucosido-glucose-1,2-enediol) may split into hydroxymethylene and 3-glucosido-arabinose, and this latter product in turn may yield 2-glucosido-erythrose and hydroxymethylene. Maltose-2,3-enediol (4-glucosido-glucose-2,3-enediol) may split into 2-glucosido-erythrose and glycol aldehyde. The 2-glucosido-erythrose formed in both cases may undergo hydrolysis into erythrose and glucose.

6. In its alkaline decomposition by the above mechanism the maltose molecule tends to form one molecule of glucose (*i.e.*, one-half of the maltose molecule), one molecule of erythrose and two molecules of hydroxymethylene. Under these experimental conditions glucose is the only one of these products which will form lactic acid in alkaline solution. As shown experimentally the yields of this acid should tend toward a value one-half that of an equivalent solution of glucose.

7. Pyruvic aldehyde is derived from glyceric aldehyde, which must be derived from glucose or any possibly formed arabinose. Since erythrose and hydroxymethylene do not yield pyruvic aldehyde, the experimental yields of pyruvic aldehyde osazone may be less than those of equivalent solutions of glucose, *i. e.*, should tend toward one-half the values obtained from the hexose. This was found to be the case.

8. Formic acid may be obtained from the two molecules of hydroxymethylene, erythrose (the alkaline glycol aldehyde of these experiments)

and glucose. These combined sources should yield more formic acid than an equivalent solution of glucose. This was found to be true.

9. Acetic acid is obtained in much smaller amounts from glucose than it is from erythrose. On the basis of the above-outlined decomposition of maltose, less acetic acid should be obtained from it than from glucose. Our data are in harmony with this point of view.

10. An experiment was made with maltose in the presence of phenylhydrazine at the lower alkalinities, seeking mannose hydrazone as an index of hydrolysis, a control being run with glucose. Mannose hydrazone was first obtained from maltose in eleven days, at 25°; after nineteen days the production reached a constant value. The hydrazone was obtained between 0.05–0.42 N potassium hydroxide. The presence of mannose is thought to be due to its formation from the glucose obtained by the hydrolysis of maltose or of 4-glucosido-mannose at the lower alkalinities.

11. The assumption of the presence of glucosido-hexose enediols and their degradation products in alkaline solutions of maltose seems to be in harmony not only with our experimental data, but also with those of Lewis and Buckborough,[1] and Glattfdd and Hanke.

12. Our data seem to be in harmony with the view that the two kinds of decomposition open to the maltose molecule—enediolic splitting and hydrolysis—go on simultaneously in alkaline solution, but whereas the former is a rapid function of the time, the latter is a very slow one.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

ACETYL CHOLINE CHLORIDE

BY LAUDER W. JONES AND RANDOLPH T. MAJOR

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Choline and its esters have achieved considerable importance in recent years due to their property of producing a marked vasodilation[1] and also because it has been shown that they are normally present in the serous coat of the intestine and probably are the normal peristaltic hormones.[2] The acetyl derivative is especially interesting since it has been found that it possesses a depressor effect 100,000 times as great as that produced by choline itself and yet it is only three times as toxic as this substance.[3]

Salts of acetyl choline have been found in certain natural products.[4] Baeyer and later Nothnagel synthesized the chloride by acetylating

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[1] Fraenkel, "Arzneimittel-Synthese," Julius Springer, Berlin, 1927, p. 336.

[2] Le Heux, *Arch. ges. Physiol.* (*Pflüger's*), 173, 8 (1918).

[3] Hunt and Taveau, *U. S. Hyg. Lab. Bull.*, No. 73 (1911); Hunt, *Pharmacol.*, 7, 301 (1915).

[4] Ewins, *Biochem. J.*, 8, 44 (1914); Boruttau and Cappenburg, *Arch. Pharm.*, 259, 33 (1921); *C. A.*, 15, 2692 (1921).

choline chloride with acetyl chloride.[5] Fourneau and Page have made acetyl choline chloride by treating trimethylamine with chloro-ethyl acetate,[6] and recently Abderhalden and Paffrath have obtained small yields of acetyl choline by the action of sodium acetate on choline in the presence of an enzyme.[7]

However, none of these investigators seem to have isolated pure acetyl choline chloride, analyzed it and determined its physical properties. Fourneau and Page unsuccessfully attempted to obtain the pure salt by recrystallizing the product formed by the interaction of trimethylamine and chloro-ethyl acetate. They used a methanol-acetone solution as a crystallizing medium, but found that acetyl choline chloride was hydrolyzed in this process.[6] Later Hunt reported that a solution of acetyl choline chloride in ethyl alcohol decomposed extremely slowly.[8]

Due to the rather widespread use of acetyl choline chloride in pharmacological investigations, it was thought that it might be of interest to isolate the pure salt, to determine its melting point and its other properties. This has been done and it has been possible to corroborate the statement made by Hunt that the compound is not appreciably hydrolyzed when it is dissolved for a short time in ethyl alcohol. Also because of the interest in this substance it was thought that another method of synthesizing it would be of value.

Accordingly, the hydrochloride of dimethylamino-ethyl acetate has been prepared from dimethylamino-ethyl alcohol and acetyl chloride, according to the equation

$$(CH_3)_2NC_2H_4OH + CH_3COCl \longrightarrow (CH_3)_2NHClC_2H_4OCOCH_3$$

Alkali converted this into its free base. This compound had previously been prepared by methylating amino-ethyl acetate, but only its physiological properties were described.[9] Treatment of dimethylamino ethyl acetate with methyl iodide gave acetyl choline iodide

$$(CH_3)_2NC_2H_4OCOCH_3 + CH_3I \longrightarrow (CH_3)_3NIC_2H_4OCOCH_3$$

from which the chloride was obtained by shaking a solution of the iodide in alcohol with silver chloride. Acetyl choline chloride was found to be a white hygroscopic solid melting at 151°. Prom this the chloroplatinate was prepared; the temperature at which decomposition occurred, 227°, corresponded rather closely to the temperature of decomposition, 223–224°, assigned by Nothnagel[5] to the chloroplatinate of acetyl choline,

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[5] Baeyer, *Ann.*, 142, 325 (1867); Nothnagel, *Arch. Pharm.*, 232,265 (1894).

[6] Fourneau and Page, *Bull. soc. chim.*, [4], *15*, 552 (1914).

[7] Abderhalden and Paffrath, *Fermentforschung*, 8, 299 (1925); C. A., 19, 2532 (1925).

[8] Hunt, *Pharmacol.*, *7*, 306 (1915).

[9] Rawita-Witanowski, *Travaux et Publ. de l'Inst. M. Nencki*, 36 (1924); *Ber. ges. Physiol. exptl. Pharmakol.*. 32, 675 (1925).

hut differed markedly from the value 256–257° given to this compound by Ewins.[10] A chloro-aurate of acetyl choline was also prepared by the method described by Baeyer[6] and later by Nothnagel.[5] The analysis of this compound agreed with that of acetyl choline chloro-aurate and all of its properties corresponded with those ascribed to this substance by Baeyer and Nothnagel except that our acetyl choline chloro-aurate melted at 168–169° while Nothnagel[6] found the melting point to be 154–155°. The reason for this difference in the melting points of these apparently otherwise identical chloro-aurates is not clear but it is well known that, due to different physical modifications, the melting point often is a criterion of little significance when one is investigating salts such as chloro-aurates and chloroplatinates.[11]

Experimental Part

Preparation of Dimethylamino-ethyl Acetate, $(CH_3)_2NC_2H_4OCOCH_3$.—To a solution of 0.2 of a mole of acetyl chloride in dry ether was slowly added, under a reflux condenser, 0.2 of a mole of dimethylamino-ethyl alcohol (Eastman Kodak Company). There was a vigorous reaction and a white solid formed at once. The solid was collected on a filter and dissolved in water. This solution was extracted with ether to remove any excess of acetyl chloride, after it had been made slightly more acidic with a little hydrochloric acid, in order more readily to hold all of the amine in the aqueous layer. More ether was then added and, while it was kept cold and stirred, the solution was made basic to phenolphthalein with solid potassium carbonate and a little caustic soda. The ether layer was separated and the aqueous solution was repeatedly extracted with ether. The ether extracts were combined and dried with anhydrous potassium carbonate. Fractional distillation yielded dimethylamino-ethyl acetate as a colorless oil; b. p. (80 mm.) 86–88"; yield, 47%.

Hydrochloride.—Dry hydrogen chloride was passed into a solution of dimethylamino-ethyl acetate in anhydrous ether. A white solid precipitated. It was recrystallized by dissolving it in absolute alcohol and reprecipitating it with ether; m. p. 129–130". It was very hygroscopic.

Anal. Subs., 0.2038: AgCl, 0.1752. Calcd. for $C_6H_{14}O_2NCl$; Cl, 21.18. Found: Cl, 21.31.

Preparation of Acetyl Choline Iodide, $(CH_3)_3NC_2H_4OCOCH_3$.—To a solution of 0.02 of a mole of dimethylamino-ethyl acetate in dry ether was added 0.02 of a mole of methyl iodide. A white solid at once formed. This solid was recrystallized from hot absolute alcohol; m. p. 160–162°; yield, 90%.

Anal. Subs., 0.2297: AgI, 0.1962. Calcd. for $C_7H_{16}O_2NI$: I, 46.40. Found: I, 46.25.

Preparation of Acetyl Choline Chloride, $(CH_3)_3NClC_2H_4OCOCH_3$.—A concentrated solution of acetyl choline iodide in warm absolute alcohol was shaken with a slight excess of silver chloride until the solution gave no further test for the iodide ion. The silver salts were removed by filtration and acetyl choline chloride was precipitated as a white solid by adding dry ether to the filtrate. In order to rid this solid of a trace of silver chloride it was added to some absolute alcohol which had previously been saturated

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[10] Ewins, *Biochem. J.*, 8, 48 (1914).

[11] F. Beilstein, "Handbuch der organischen Chemie," Julius Springer, 1922, 4th ed., Vol. 4, pp. 204, 280; Willstatter, *Ber.*, 35, 2700 (1902).

with hydrogen sulfide. The silver precipitated as silver sulfide but the acetyl choline chloride readily dissolved. In order to separate the silver sulfide more easily, activated charcoal which previously had been washed with absolute alcohol was added. The mixture was shaken for a few minutes and then filtered. Acetyl choline chloride was reprecipitated from the filtrate by the addition of dry ether; m. p. 151°; yield, 65%. It was very soluble in water and alcohol, but insoluble in ether. It was extremely hygroscopic.

Anal. Subs., 0.2344: AgCl, 0.1867. Calcd. for $C_7H_{16}O_2NCl$; Cl, 19.53. Found: Cl, 19.70.

Chloroplatinate.—The calculated amount of a concentrated solution of chloroplatinic acid in absolute alcohol was added to 0.1 g. of acetyl choline chloride in absolute alcohol. An orange-colored precipitate soon formed. It was recrystallized from hot water and then washed with water and alcohol; m. p. 227° with decomposition.

Anal. Subs., 0.1296: Pt, 0.0362. Calcd. for $C_{14}H_{34}O_4N_2PtCl_6$: Pt, 27.81. Found: Pt, 27.93.

Chloro-aurate.—To 0.46 g. of acetyl choline chloride dissolved in water was added the calculated amount of a concentrated solution of auric chloride in water. An orange-colored solid at once precipitated. It was recrystallized from hot water; m. p. 168–169°.

Anal. Subs., 0.2212: Au, 0.0894. Calcd. for $C_7H_{16}O_2NAuCl_4$: Au, 40.55. Found: Au, 40.42.

Summary

1. Dimethylamino-ethyl acetate has been prepared by adding alkali to the product formed by the interaction of acetyl chloride and dimethylamino-ethyl alcohol.

2. Acetyl choline iodide was formed when dimethylamino-ethyl acetate was treated with methyl iodide. From the iodide the corresponding chloride, chloroplatinate and chloro-aurate were made.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

PAPAVERINE: AN ATTEMPTED RÜGHEIMER SYNTHESIS

BY IVEY ALLEN, JR., AND JOHANNES S. BUCK

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A simple general synthesis of the papaverine type of alkaloid is for many reasons of great importance, particularly so as it would offer a possible means of synthesizing the tetrahydroberberine type of alkaloid.[1] The two methods[2] for synthesizing papaverine which have been worked out are probably only of scientific interest on account of the inaccessibility of the starting materials. An ideal starting point for the synthesis of isoquinoline alkaloids would be a benzoin or a benzil. Such a synthesis was attempted by Fritsch,[3] who condensed desoxyveratroin with amino-acetal and at-

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Späth and Kruta, *Monatsh.*, 50,341 (1928).

[2] Pictet and Gams, *Ber.*, 42, 2943 (1909); Buck, Haworth and Perkin, *J. Chem. Soc.*, 125,2176 (1924).

[3] Fritsch, *Ann.*, 329, 37 (1903).

tempted to cyclize the product after the method of Pomeranz.[4] No papaverine was obtained. Fritsch obtained his desoxyveratroin by a rather involved series of reactions from veratrole and dichloro-acetaldehyde, while the authors prepared this material from veratric aldehyde, via veratril.

Rugheimer and Schön[5] prepared dimethoxyisoquinoline by condensing veratrylamine with chloro-acetal and cyclizing the product, using sulfuric acid and arsenic pentoxide as cyclizing agents. In a similar manner tetramethoxydiphenylethylamine should condense with chloro-acetal to tetramethoxystilbylainino-acetaland this product be capable of cyclization to papaverine.[6] The authors undertook to investigate this possibility. It was realized at the outset that the chances were against success, as many failures of the Rugheimer synthesis are recorded, among them the failure of Salway[7] and later Rügheimer[8] to cyclize myristicylamino-acetal. In addition, it is known that papaverine is unstable to sulfuric acid above about 80%, even without the presence of oxidizing agents? However, the importance of the issue was considered to justify the attempt. The expected result was obtained, namely, that tetramethoxystilbylamino-acetal cannot be cyclized to papaverine and that, therefore, the Riigheimer synthesis is not applicable to the benzylisoquinoline alkaloids such as papaverine.

As a check on the work, the same process was carried out with the corresponding methylenedioxy derivatives, starting with piperonal in place of veratric aldehyde. Exactly parallel results were obtained, the stilbylamino-acetal being destroyed and not cyclized at the last stage.

The stages in the attempted synthesis are as follows

$(CH_3O)_2C_6H_3CHO \longrightarrow (CH_3O)_2C_6H_3CHOHCOC_6H_3(OCH_3)_2 \longrightarrow$

Veratric aldehyde Veratroin

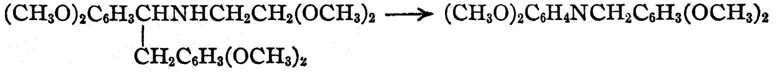
$(CH_3O)_2C_6H_3COCOC_6H_3(CH_3O)_2 \longrightarrow (CH_3O)_2C_6H_3CH_2COC_6H_3(OCH_3)_2 \longrightarrow$

Veratril Desoxyveratroin

$(CH_3O)_2C_6H_2CH_2C(NOH)C_6H_3(OCH_3)_2 \longrightarrow (CH_3O)_2C_6H_3CH_2CHNH_2C_6H_3(OCH_3)_2$

Desoxyveratroin oxime Tetramethoxydiphenylethylamine (Tetramethoxystilbylamine)

Sym.-diphenylethane is an unsuitable root for the naming of side-chain derivatives. It was, therefore, re-named "stilbane" (by analogy with stilbene) in this paper. The radical stilbyl is then $C_6H_5CH_2CHC_6H_5$ and the radical stilbylidene, $C_6H_5CH_2CC_6H_5$.



$$\underset{\textstyle CH_2C_6H_3(OCH_3)_2}{(CH_3O)_2C_6H_3CHNHCH_2CH_2(OCH_3)_2} \longrightarrow (CH_3O)_2C_6H_4NCH_2C_6H_3(OCH_3)_2$$

Tetramethoxystilbylamino-acetal **Papaverine**

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[4] Pomeranz, *Monatsh.*, 14, 116 (1893), etc.

[5] Riigheimer and Schon, *Ber.*, 42,2374 (1909).

[6] *Cf.* Staub *Helv. Chim. Acta,* **5**, 888 (1922).

[7] Salway, *J. Chem. Soc.*, 95, 1204 (1909).

[8] Riigheimer, *Ber.*, 45, 1340 (1912).

[9] Fritsch, ***Ann.***, 329, 37 (1903).

Experimental

Veratril.—Veratric aldehyde, prepared by the method of Buck and Perkin[10] was converted into veratril substantially as described by Vanzetti.[11]

Desoxyveratroin. First Method.[12]—Twenty grams of veratril, 200 cc. of alcohol, 40 g. of granulated tin and 5 cc. of saturated copper sulfate solution were heated on the water-bath for four hours, during which time 200 cc. of concentrated hydrochloric acid containing 15 cc. of copper sulfate solution was gradually added. The mixture was filtered, diluted with an equal volume of water and allowed to stand. The product which separated was filtered off and recrystallized from alcohol. It forms colorless needles melting at 107°.

Anal. Calcd. for $C_{18}H_{20}O_5$: C, 68.36; H, 6.33. Found: C, 68.31; H, 6.29.

Second Method.[13]—Seven grams of homoveratric acid (prepared by the method of Haworth and co-workers)[14] was dissolved in 20 cc. of chloroform and 5.0 g. of thionyl chloride added. The mixture was refluxed for forty minutes on the water-bath, the chloroform then distilled off and 30 cc. of carbon disulfide and 11 g. of veratrole (prepared from guaiacol and methyl sulfate) added; 12 g. of anhydrous aluminum chloride was introduced in portions through the condenser and the whole refluxed for two hours, allowed to stand for a further two hours and then treated with water. The carbon disulfide layer was separated and water added, after which steam was passed through to remove the solvent and excess veratrole. After purification from dilute alcohol, the product melted at 107° and was identical with the desoxyveratroin prepared by the first method. It corresponded exactly with the description given by Fritsch.[3]

Desoxypiperoin.—Fifty grams of piperoin (prepared after the method of Perkin),[15] 40 g. of granulated tin and 200 cc. of alcohol were heated on a steam-bath under a reflux condenser, 73 cc. of concentrated hydrochloric acid containing a little copper sulfate was added and the whole refluxed for three hours. A further 50 cc. of alcohol and 20 cc. of acid with a little copper sulfate were then added and the heating continued for one and one-half hours. On cooling, the product crystallized out. A further amount separated on diluting the liquor; yield, 23 g. Desoxypiperoin forms small white needles melting at 114° when crystallized from alcohol, in which it is sparingly soluble.

Anal. Calcd. for $C_{16}H_{12}O_5$: C, 67.61; H, 4.24. Found: C, 67.48; H, 4.40.

Desoxyveratroin **Oxime.**—Fifty grams of desoxyveratroin and 12.5 g. of hydroxylamine hydrochloride were heated with 125 cc. of pyridine on a boiling water-bath for five hours. The solution was then diluted with water to 500 cc. and allowed to stand. The oil which separated became crystalline on standing; yield, 38 g. The oxime forms fine white needles melting at 128° when crystallized from alcohol.

Anal. Calcd. for $C_{18}H_{21}O_5N$: C, 65.27; H, 6.34; N, 4.2. Found: C, 65.03; H. 6.26; N, 4.5.

Desoxypiperoin Oxhe.—Twenty grams of desoxypiperoin was heated on a water-bath for two hours with 50 cc. of pyridiie and 5 g. of hydroxylamine hydrochloride. On adding water to incipient precipitation and allowing the mixture to stand, the oxime crystallized out; yield, 19 g. Desoxypiperoin oxime crystallizes from alcohol, in which it is sparingly soluble, in colorless needles melting at 158°.

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[10] Buck and Perkin, *J. Chem. Soc.*, 125, 1678 (1924).

[11] Vanzetti, *Gazz. chim. ital.*, 57, 162 (1927).

[12] Cf. Zinin, *Ann.*, 119,177 (1861); Wachter, *Ber.*, 25, 1727 (1892).

[13] *Cf.* Cain, Simonsen and Smith, *J. Chem. Soc.*, 103,1035 (1913).

[14] Haworth and co-workers, *ibid.*, 125, 1686 (1924).

[15] Perkin, *ibid.*, 59, 150 (1891).

Anal. Calcd. for $C_{16}H_{13}O_5N$: C, 64.21; H, 4.35; N, 4.7. Found: C, 64.40; H, 4.51; N, 4.7.

Tetramethoxystilbylamine.[16]—Twenty grams of desoxyveratroin oxime dissolved in 200 cc. of alcohol was treated while hot with 800 g. of 3.5% sodium amalgam, and 100 cc. of glacial acetic acid added in portions during one hour, the mixture being kept hot and water being added as required to keep the sodium acetate formed in solution. When cool, the mixture was diluted to 400 cc. with water and allowed to stand overnight to permit the separation of unchanged oxime. After removing the mercury and filtering, a slight excess of ammonia was added. The resulting precipitate was filtered off and recrystallized; yield, 15 g. Tetramethoxystilbylamine forms glistening plates melting at 107° when crystallized from water, in which it is sparingly soluble. It is soluble in cold alcohol and benzene, sparingly soluble in ether and insoluble in petrol ether. The hydrochloride forms white crystals melting at 195°. The hydrobromide is pale yellow and melts at 241°.

Anal. Calcd. for $C_{18}H_{23}O_4N$: C, 68.14; H, 7.25; N, 4.4. Found: C, 68.06; H, 7.48; N, 4.5.

Acetyl Derivative.—Acetylation by means of acetic anhydride gave the acetyl compound, which crystallized from alcohol in a felted mass of colorless needles melting at 160–162°.

Anal. Calcd. for $C_{20}H_{25}O_5N$: N, 3.9. Found: N, 4.0.

Dimethylenedioxystilbylamine.—This compound was prepared in the same manner as the foregoing tetramethoxy compound, the same quantities being used; yield, 17 g. It is best purified by recrystallizing the hydrochloride from alcohol and then suspending the salt in hot water and adding an excess of ammonia. The base is readily soluble in cold alcohol and benzene and sparingly soluble in ether and petrol ether. Recrystallized from water, in which it is sparingly soluble, it forms long shining needles melting at 111°. The hydrochloride forms colorless needles melting at 245".

Anal. Calcd. for $C_{16}H_{15}O_4N$: C, 67.38; H, 5.26; N, 4.9. Found: C, 67.79; H, 5.44; N, 5.2.

Acetyl Derivative.—The acetyl derivative prepared by acetylation of the base with acetic anhydride crystallizes from dilute acetic acid in small clusters of tiny colorless needles melting at 141°.

Anal. Calcd. for $C_{18}H_{17}O_5N$: N, 4.3. Found: N, 4.1.

Tetramethoxystilbylamino-acetal.—Three grams (1 mole) of tetramethoxystilbylamine and 1.0 g. (0.5 mole) of bromo-acetal were heated slowly in an oil-bath until the temperature reached 150° (forty-five minutes). After cooling, the mixture was sludged with ether and filtered. The precipitate of tetrarnethoxystilbylamine hydrobromide was filtered off with suction and washed with ether. The filtrate and washings were united and the ether was evaporated. The product, like practically all compounds of this class, formed a reddish oil which could not be crystallized and which gave no crystalline derivatives. In the presence of reagents it gave back the original amine by fission with rather unusual ease. The material obtained was used directly for subsequent experiments.

Dimethylenedioxystilbylamino-acetal.—This was prepared in the same manner as the foregoing tetramethoxy compound except that the heating was carried out at 125°. It also forms a reddish oil, uncrystallizable and giving no crystalline derivatives.

Action of **Cyclizing** Agents on **Tetramethoxystilbylamino-acetal.**—The method of

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[16] *Cf.* Goldschmidt and Polonowska, Ber., 20, 492 (1887); Strandmark. *Svensk Kem. Tid.*, 18, 3 (1906).

investigation was to take 1.5 g. of tetramethoxystilbylamino-acetal and 2.0 g. of arsenic pentoxide, together with 20 cc. of sulfuric acid, and to heat the mixture on the water-bath for thirty minutes. The reaction mixture was poured into water and neutralized. Nothing but black amorphous material which could not be purified and from which no derivatives were obtainable was ever found. The starting material was evidently completely destroyed. Acid of 30, 50, 65 and 75% strength was tried in the hot as well as 65 and 75% acid in the cold. Dimethylenedioxystilbylamino-acetal was completely destroyed by 75% sulfuric acid and arsenic pentoxide in the cold.

It is, therefore, evident that the stilbylamino-acetals are unstable under the rather drastic treatment required to produce a Riigheimer cyclization and that further, work along these lines would be profitless.

Summary

Tetramethoxystilbylamino-acetal and dimethylenedioxystilbylamino-acetal were prepared from veratric aldehyde and piperonal, respectively, in an attempt to synthesize papaverine and the corresponding dimethylenedioxybenzylisoquinoline. The stilbylamino-acetals were found to be unstable to the usual cyclizing agents, thus precluding the synthesis of papaverine and its homologs by this method.

DURHAM, NORTH CAROLINA

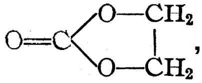
[CONTRIBUTION NO. 19 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY]

STUDIES ON POLYMERIZATION AND RING FORMATION.
III. GLYCOL ESTERS OF CARBONIC ACID

BY WALLACE H. CAROTHERS AND F. J. VAN NATTA

RECEIVED JULY 24, 1929 PUBLISHED JANUARY 8, 1930

The glycol esters of dibasic acids described in a previous paper[1] are all highly polymeric. This was expected from the generalization[2] that bifunctional reactions which, if intramolecular, could lead only to larger-than-6 rings proceed intermolecularly. It seemed desirable to examine an homologous series of similar compounds in which the length of the structural unit might be as short as 5 or 6 atoms, since in these cases reaction should be intramolecular and the products monomeric, and in the longer chains of the same series reaction should be intermolecular and the products polymeric.

Such a series is found in the glycol esters of carbonic acid. The first member of this series, ethylene carbonate, , has long been known.[3] It is a crystalline solid which boils at 238° and it is definitely

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[1] Carothers and Arvin, THIS JOURNAL, 51, 2560 (1929).

[2] Carothers, *ibid.*, 51, 2548 (1929).

[3] Nemirowski, *J. prakt. Chem.*, [2] **28**, 439 (1883); *Chem. Zentr.*, 23 (1884).

established to be the monomeric 5-ring by both cryoscopic and vapor density data.[4]

We have now prepared the trimethylene, tetramethylene, hexamethylene, decamethylene, diethylene and p-xylylene esters of carbonic acid. The properties of these esters, together with the apparent mean molecular weights determined by cryoscopic and ebullioscopic methods, are indicated in Table I. The analytical compositions of all these esters correspond with the formulas of their structural units $—O—(CH_2)_n—CO—$, but where the length of the chain of this unit is 5 or 6, only one such unit is present in a molecule of the ester. On the other hand, where the length of the chain of the structural unit is 7, 8, 9 or 13, eight to twenty-two structural units are present in each molecule. The method of preparation and the analytical compositions of the polymeric esters indicate a structure which may be represented by the general formula $—O—(CH_2)_n—O—CO—O—(CH_2)_n—O—CO—O—(CH_2)_n—O—CO—O—(CH_2)_n—O—CO—$, etc. To complete this formula, it is necessary to discover whether the valences at the ends of the chains are saturated mutually with the formation of a ring, or are saturated by univalent groups to give open chains. The 7-, 8-, 9- and 13-membered rings which might be formed in this reaction are not found, and there is no reason to suppose that much larger rings would be formed more readily. For some poly-esters similar to those described here we have direct experimental proof of the open-chain structure. It seems quite certain, therefore, that these polycarbonates are also open chains. From the method of preparation it follows that the ends of the chains must bear hydroxyl groups (from an extra molecule of glycol) or carbethoxy groups (from an extra molecule of ethyl carbonate). In this connection it is interesting to observe that when an excess of ethyl carbonate was used in the preparation of hexamethylene carbonate, pure dicarbethoxyhexane, $C_2H_5O—CO—O(CH_2)_6O—CO—OC_2H_5$, was isolated, and an oil which, judging by its composition, was composed chiefly of $C_2H_5-O—CO—O(CH_2)_6O—CO—O(CH_2)_6O—CO—O(CH_2)_6O—CO—OC_2H_5$.

Properties of the **Polycarbonates.**—The physical properties of these polycarbonates again illustrate the fact that neither melting points nor solubilities offer any general criteria of molecular size.

In this connection trimethylene carbonate is of especial interest since it has been obtained in both the monomeric form and a form in which the degree of polymerization is 38–45. The monomeric form is hygroscopic and is soluble in water, benzene and alcohol, but only slightly soluble in ether and ligroin. The polymeric form is not soluble in water and alcohol, but is still soluble in benzene. Solubility here diminishes with considerable increase in molecular size, but it does not disappear. Practically all the polymeric esters described in this and the previous paper

[4] Vorländer, *Ann.*, 280, 186 (1894).

TABLE I

GLYCOL ESTERS OF CARBONIC ACID

Names of carbonates	Formula of structural unit	No. of atoms in chain of structural unit	Anal. calcd. for structural unit	Analysis found,[a]	Mol. wt. obs.	Method	Av. no. of structural units per molecule	Physical properties
Ethylene	$-O(CH_2)_2-O-\underset{\underset{O}{\|}}{C}-$	5	C 40.91 H 4.54	41.07[b] 4.88	90 93b 76	F. p.. C_6H_5OH[b] Vapor density	1	M. p. 39°[b] B. p. 238°
Trimethylene (monomeric)	$-O(CH_2)_3-O-\underset{\underset{O}{\|}}{C}-$	6	C 47.06 H 5.92	46.97 47.14 5.96 5.98	105 114 112 114	F. p. C_6H_6 B. p. C_6H_6	1	Colorless needles M. p. 47–8° B. p. 135° at 4 mm.
Trimethylene (polymeric)	$-O(CH_2)_3-O-\underset{\underset{O}{\|}}{C}-$	6	C 47.06 H 5.92	47.06 47.08 6.01 6.19	4670 3880	B. p. C_6H_6	38–45	Glass gradually changes to powder
Tetramethylene	$-O(CH_2)_4-O-\underset{\underset{O}{\|}}{C}-$	7	C 51.71 H 6.94	52.18 52.32 7.05 7.06	1450 1400 1350 1310 1290 1370	B. p. C_6H_6. F. D. C_6H_6	11–12	Powder M. D. 59°
Pentamethylene	$-O(CH_2)_5-O-\underset{\underset{O}{\|}}{C}-$	8	C 55.96 H 7.75	55.29 55.47 7.90 7.83	2840 2830 2550	B. p. C_6H_6	20–22	Powder M. p. 44–6°
Hexamethylene	$-O(CH_2)_6-O-\underset{\underset{O}{\vert}}{C}-$	9	C 58.33 H 8.33	58.58 58.54 8.46 8.21	2740 2970 2610	B. p. C_6H_6	18–21	Horny and elastic M. p. 55–60'
Decamethylene	$-O(CH_2)_{10}-O-\underset{\underset{O}{\|}}{C}-$	13	C 65.96 H 10.07	65.80 66.04 10.18 10.10	1880 1800 1810 1640 1770 1830	B. p. CsHa F. D. C_6H_6	8–10	Powder M. D. 55°
Diethylene	$-O(CH_2)_2-O-(CH_2)_2-O-\underset{\underset{O}{\|}}{C}-$	8	C 45.44 H 6.11	45.53 45.33 6.30 6 38	1540 1550	B. p. C_6H_6	12	Sirup
p-Xylylene (soluble)	$-O-CH_2C_6H_4CH_2-O-\underset{\underset{O}{\vert}}{C}-$	9	C 65 84 H 4.91	65 81 66 00 5 60 5 63	840 780 810	B. p. $C_2H_4Cl_2$	5	Powder M. p. 137–8°
p-Xylylene (insoluble)	$-O-CH_2C_6H_4CH_2-O-\underset{\underset{O}{\vert}}{C}-$	9	C 65.84 H 4 91	65 02 65 03 5.29 5.19	1010 1030	M. p. camphor	6	Powder M. p. 177–85°

[a] The analyses were carried out by the Pregl micro method

[b] Vorländer, *Ann.*, 280, 187 (1894).

are insoluble in water and alcohol, but soluble in chloroform and somewhat soluble in acetone. Those poly-esters in which the structural units contain polymethylene chains, $(CH_2)_x$, in which x is greater than 3–5, show great solubility in benzene.

Poly-esters of high molecular weight may be either liquid (diethylene carbonate, ethylene malonate,[1] decamethylene phthalate[1]) or solids. Most of the solid poly-esters are *crystalline.* These crystalline poly-esters differ from analogously constituted crystalline esters of low molecular weight in that the crystals are always microscopic. In some cases it is not possible to decide even by microscopic examination whether these solid polymers are crystalline, but x-ray examination always shows definite crystallinity. Thus hexamethylene carbonate was an opaque, tough, horny material with considerable elasticity. Nevertheless, it had a fairly definite melting point and it gave a quite sharp x-ray diffraction pattern (Fig. 3).

The following generalizations concerning the influence of the structure of the structural units of poly-esters on their physical properties can now be offered. As the lengths of the poly-methylene chains, $(CH_2)_x$, which separate the ester groups increase, solubility in organic solvents increases and viscosity of the molten ester diminishes. This would be expected from the fact that carbonyl groups contribute much more heavily to intermolecular association forces than do methylene groups. With one exception (ethylene malonate[1]) all of the linear poly-esters in which the ester groups are separated only by polymethylene chains, $(CH_2)_x$, are solids. Less symmetrical linear polyesters such as the alkylene phthalates are resins (transparent glasses or sirups). The solid poly-esters when melted and then cooled yield opaque masses. These may be brittle and porcelain-like or soft and waxy. The waxy quality increases with the lengths of the polymethylene chains just as it does in the glycols and the acids from which the poly esters are derived.

The problem of the more precise expression of the relationship between the structure and the properties of high polymers is complicated by the fact that some of the properties of this class of substances which are of the greatest practical importance and which distinguish them most sharply from simple compounds cannot be accurately measured and indeed are not precisely defined. Examples of such properties are toughness and elasticity. We have found these two properties in only one of the poly-esters which we have prepared. This poly-ester is hexamethylene carbonate. Like pentamethylene and decamethylene carbonates, this material is crystalline; it has a fairly definite melting point (55–60°) and it gives a sharp x-ray diffraction pattern (see Fig. 3). But the higher and lower members of this series separate from solution as powders, while hexamethylene carbonate separates in the form of rubbery flakes. It is not yet certain that this peculiar combination of properties is inherently associated with the molecular structure of this particular ester (*i. e.*, with the linear union of a large number of the structural units —CO—O—$(CH_2)_6$—O—) rather than with some accidental features of its formation which may have been absent in the preparation of other members of the series, but the important problem of the relationship between chemical or physical structure and rubber-like properties is so poorly provided with material suitable for inductive argument that the discovery of a new synthetic and analytically homogeneous material exhibiting these properties is of some significance. So far as we are aware there is nothing in current theories which would lead one to expect that polymeric hexamethylene carbonate would be elastic.

As indicated above, high polymers, like materials of low molecular weight, may show great variety in certain physical properties—they may be either liquids or high-melting solids; they may show slight or very great solubility. The following properties, however, are inherently associated with the highly polymeric state.

(1) Lack of Volatility.—None of the poly-esters which we have prepared can be volatilized as such even at very low pressures and high temperatures. Volatility diminishes continuously with increase in molecular size due to the increase in intermolecular forces. It is probably true in general that compounds whose molecular cohesions lie above 75,000 cal. (the heat of separation of a carbon–carbon bond) cannot be distilled. The calculated molecular cohesion (about 250,000 cal.),[5] of our poly-esters lie far above this value.

(2) Viscosity in Liquid State.—This would be expected to increase with the intermolecular forces and so with molecular size. All of the poly-esters which we have studied are extremely viscous in the molten state.

(3) Micro-crystallinity in the Solid State.—This has been referred to above. In this connection it is interesting to observe that considerable difficulty was experienced in preparing and keeping crystals of monomeric trimethylene carbonate sufficiently small to yield a powder diagram in an x-ray diffraction experiment. On the other hand, it has not been possible to prepare macroscopic crystals of any polymeric ester.

Trimethylene Carbonate.—Among all the esters formed from bifunctional reactions which we have studied, trimethylene carbonate and ethylene oxalate[6] present the peculiar property of exhibiting reversible transformation between a monomeric and a polymeric form. These monomeric esters contain 6-membered rings. The polymerization of trimethylene carbonate is brought about by heating and is catalyzed by a trace of potassium carbonate. The polymer is a perfectly colorless, transparent

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[5] Meyer and Mark, *Z. angew.* Chem., 41,943 (1928).

[6] See Bischoff, Ber., 40, **2803** (1907). Our own studies of alkylene oxalates will be described later.

glass, which on long standing becomes opaque (crystallization). X-ray diffraction patterns of the monomeric and polymeric forms are shown in Figs. 1 and 2. The polymer has the same apparent analytical composition as the monomer. Its degree of polymerization as measured by molecular weight determinations in boiling benzene is 3845. On heating *in vacuo,* it distils and the distillate is found to be the monomeric form. Examination of the literature shows that the property of undergoing reversible polymerization is common to many 6-rings containing ester linkages. Thus, the lactones of δ-hydroxyvaleric acid and of the hydroxyethyl ether of glycolic acid polymerize on heating[7] and so does glycolide.[8] The action of heat on lactic acid leads to polylactyl lactic acids, and these on further heating are converted to the 6-ring lactide.[9]

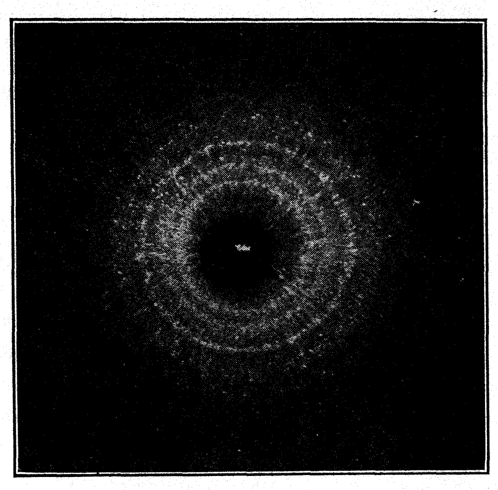

Fig. 1.—Monomeric trimethylene carbonate (Mo radiation). The intensity of the numerous outer rings is weak and these do not appear in the reproductions.

The unique position occupied in this respect by 6-rings containing an ester linkage is indicated by the following facts. No record of the polymerization of *a* γ-lactone (5-ring) is found. Our own attempts to polymerize ethylene carbonate (5-ring) were unsuccessful. The polyesters which we have prepared and in which the length of the chain of the structural unit is greater than 7 are not depolymerized on heating. The monomeric form of none of these esters is known.

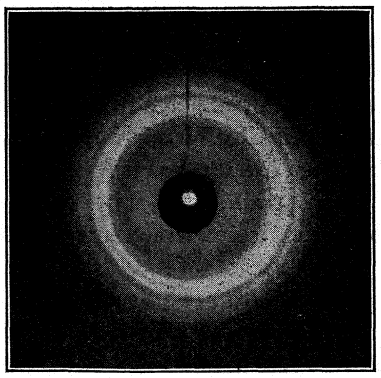

Fig. 2.—Polymeric trimethylene carbonate (Cu radiation).

In an attempt to force the depolymerization of tetramethylene carbonate, it was heated above 300° at 0.9 mm. This caused it to decompose with the evolution of considerable gas. From the dis-

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[7] Hollo, *Ber.,* 61, 895 (1928).

[8] Bischoff and Walden, *Ann.,* **279,** 45 (1894).

[9] Dietzel and Krug, *Ber.,* 58, 1307 *(1925).*

tillate was isolated a very small amount (about 1% of the calculated) of a crystalline solid having the analytical composition of tetramethylene carbonate. Molecular weight determinations indicated that it is a dimer: $\overline{COO(CH_2)_4OCOO(CH_2)_4O}$. The absence of a monomer was not definitely established, but it could only have been present in very small amount. Thus, the behavior of polymeric tetramethylene carbonate is very different from that of its next lower homolog.

In the self-esters of some of the higher ω-hydroxy fatty acids, $HO(CH_2)_x$-COOH, both the monomeric lactones and the poly-esters are known.[10] The poly-esters, however, are not depolymerized on heating, and the poly-esters, not the lactones, are formed on heating the acids.

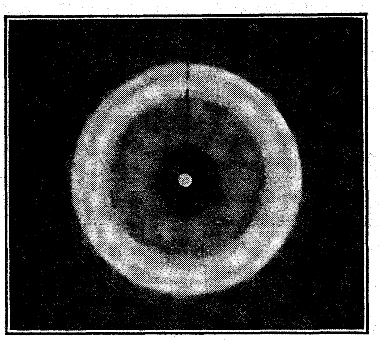

Fig. 3.—Hexamethylene carbonate (Cu radiation).

These facts, together with others which will be discussed later, indicate clearly that poly-esters formed by bifunctional reactions in which the length of the structural unit is greater than 6 atoms are the direct result of intermolecular condensation (C polymerization).[2] The formation of polymeric trimethylene carbonate from its monomer is obviously A polymerization, and the same is true of the polymerization of lactides and of 6-lactones.

A fairly satisfactory explanation of these peculiarities may be found in the Mohr theory,'' which has proved adequate to explain all of the previously observed influences of structural features on the course of bifunctional reactions.[2] In accordance with the terms of this theory, 5-rings will be readily formed and very stable since they are free from strain. The formation of seven-membered and larger rings by bifunctional reactions is very improbable, but such rings once they are formed will be quite stable, since they too are practically free from strain. Six-rings will be readily formed, but they present the possibility of strains which are absent or present only to a diminished degree in larger rings. Thus, the Mohr theory predicts the possible existence of two cyclohexanes (cis and *trans)* but only one is known, However, where structural features would preclude the possibility of the interconversion of these two forms, as in decalin, both forms are known. It is concluded, therefore, that in simple 6-rings, such as cyclohexane, equilibrium with reversible interconversion

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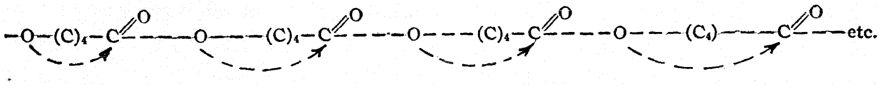
[10] Ruzicka and Stoll, *Helv. Chim. Acta,* 11, 1159 (1928); Lycan and Adams, THIS JOURNAL, 51, 625 (1929); Chuit and Hausser, *Helv. Chim. Acta, 12,* 463 (1929); Lycan and Adams, THIS JOURNAL, 51, 3450 (1929).

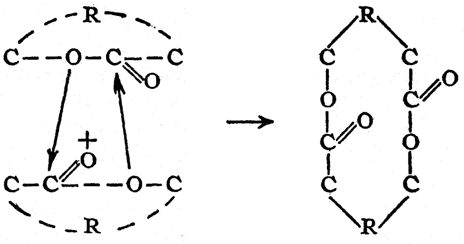
[11] Mohr, *J. prakt. Chem.,* 98,348 (1918).

of the two forms exists. At every such interconversion the molecule must pass through a position of considerable strain. This picture presents the features necessary to rationalize the peculiar position of 6-membered ester rings. A poly-ester in which the recurring structural unit is a chain of six atoms would be readily converted into the corresponding monomeric 6-ring by a process of ester interchange, as indicated below:



If the chain of the structural unit were longer than 6 atoms, this reaction would be less probable for the same reason that the higher ω-hydroxy fatty acids do not yield lactones, *i.* e., the number of points of rotation in the chain between carbonyl and alcoholic oxygen are so numerous that the probability of close intramolecular approach of these groups is very low.

The polymerization of the 6-ring esters seems also to involve ester interchange. This process may involve the coalescence of two such rings, as indicated below



The resulting 12-ring might then coalesce with another six-ring, and so on, with the formation of very large rings. It is possible also that traces of water may intervene at some stage in the process and that the large molecules produced are open rather than closed chains. In any event the peculiar mobility of the 6-ring esters may be ascribed to the fact that these rings are subject to strains, and that the strains may be relieved by an ester interchange resulting in an enlargement of the molecule.

The precise mechanism of the polymerization of the 6-membered ester rings shares to a certain extent the obscurity which is common to most cases of A polymerization, but further attention is being devoted to this problem and the study is being extended to the corresponding amides. In this connection the analogy which exists between lactides and diketopiperazines on the one hand, and poly-esters and polypeptides on the other hand, is of especial interest because of its possible relationship to the structure of proteins.

Dimeric Tetramethylene Carbonate.—The dimeric tetramethylene carbonate referred to above deserves special mention. There can be little doubt that it is a 14-membered cyclic ester, and as such it represents a class of compounds of which few members are known. Other dimeric cyclic esters have been obtained and will be described in later papers.

Previous Work on the Carbonates of **Dihydric** Alcohols.—Reference to ethylene carbonate has already been made. Carbonates of the three dihydroxybenzenes were prepared by Bischoff and v. Hedenström.[12] The carbonate of catechol is apparently monomeric since it can be distilled. The *m*-phenylene carbonate is a non-volatile, brown, glassy material of uncertain melting point (197–202°) and low solubility, and the corresponding para compound shows similar properties. These two compounds are evidently polymeric.

Experimental Part

Preparation of Carbonates.—The carbonates here described were all prepared by ester interchange (alcoholysis) between the glycol and ethyl carbonate. This reaction proceeds very smoothly in the presence of an alkaline catalyst and may be forced to completion; the process need not be modified to take into account the solubility of the resulting ester, as is necessary when phosgene and the glycol are used as starting materials.

Trimethylene Carbonate.—A mixture of **60.8** g. **(0.8** mole) of trimethylene glycol, **114 g. (16%** excess) of ethyl carbonate and a small cube of sodium was warmed in a Claisen flask until the sodium had completely dissolved. The flask was then immersed in an oil-bath at 130°. During three hours the temperature was allowed to rise to 170°. The evolved alcohol condensed and collected weighed 69.1 g. or 94% of the calculated.

The oily residue was dissolved in benzene, washed twice with 20-cc. portions of water and dried over calcium chloride. After removal of the solvent, the residue was subjected to vacuum distillation. **A** small initial fraction, b. p. 120–135° at **20 mm.,** was unchanged glycol. The pure trimethylene carbonate then distilled fairly constantly; b. p. 160–165° at **6 mm.**; 135° at **4 mm.,** 105° at **0.2** mm.; weight **53** g., or **65%** of the calculated. It completely crystallized in the receiver; recrystallization from absolute ether produced colorless needles, m. p. 47–48°. This hygroscopic ester is very soluble in benzene, alcohol and water and slightly soluble in ether and ligroin. It decomposes on distillation at ordinary pressure. This ester gave a sharp x-ray powder diagram (Fig. **1)** slightly scattered due to the difficulty of obtaining sufficiently small crystals. For analysis, see Table I.

Polymerization of Trimethylene Carbonate.—In the distillation of trimethylene carbonate it was frequently observed that the distilling residue was very thick and viscous while the warm distillate was comparatively thin and mobile. The distillation of **53** g. of trimethylene carbonate was interrupted while still incomplete. The distillate was monomeric trimethylene carbonate, m. p. 48°. The undistilled residue **(15.6** g.) was very viscous even when hot and it cooled to a colorless sticky resin. Molecular weight determinations showed it to be polymeric; molecular weight in boiling benzene, found: **2390,2320.**

This residue was distilled at **10 mm.** It yielded **13.6** g. of monomeric trimethylene carbonate (observed b. p. 150–190") which completely crystallized on cooling; mol. wt., calcd. for monomeric trimethylene carbonate: **102.** Found: (in boiling benzene) **115, 118.**

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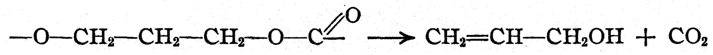
[12] Bischoff and v. Hedenstrom, **Ber., 35,3431** (1902).

The tarry residue (1.7 g.) remaining in the flask was insoluble in the common organic solvents.

A trace (0.1%) of finely powdered anhydrous potassium carbonate was added to a sample of the pure crystalline monomeric ester and the mixture was heated at 130°. After shaking and heating for ten minutes the mixture suddenly became very viscous and a slight amount of gas was evolved. After five hours of heating the colorless product formed a clear glassy mass on cooling; mol. wt., found: (in boiling benzene) 9670, 3880. For analysis see Table I. After standing for a week, this glassy polymer became opaque and x-ray examination showed it to be crystalline (Fig. 2).

Under similar conditions (temp. 130°; time of reaction, four hours) ethylene carbonate did not polymerize.

When polymeric trimethylene carbonate was heated to 210° at ordinary pressure, it was decomposed. Allyl alcohol was identified as one of the products of this reaction by its boiling point and by the melting point of its phenylurethan. This fact indicated decomposition according to the scheme



$$-O-CH_2-CH_2-CH_2-O-C{=}O \longrightarrow CH_2{=}CH-CH_2OH + CO_2$$

The allyl alcohol isolated accounted for only about 25% of the ester decomposed. Higher boiling unsaturated materials present in the products of this reaction were not identified.

Tetramethylene Carbonate.—This was prepared from 9.0 g. of tetramethylene glycol, to which a small piece ($2\ mm.^3$) of sodium had been added and 11.8 g. of ethyl carbonate. The mixture was heated to 120° and then the temperature was allowed gradually to rise to 160° during seven hours. The distillate was poured back several times to insure complete reaction of the ethyl carbonate. From the distillate was isolated 5.7 g. or 62% of the calculated amount of ethyl alcohol.

The non-volatile reaction product was dissolved in benzene and the solution washed with water, dilute hydrochloric acid and water. It was dried with calcium chloride and the solvent was removed by distillation. On heating the residue in *vacuo* there was obtained a very small amount of distillate boiling at 100–110° at 1 mm. This was chiefly unchanged tetramethylene glycol since it gave a di-*p*-nitrobenzoate, m. p. 175°. No further distillation could be effected when the bath was heated to 250° and the pressure reduced to 0.2 mm.

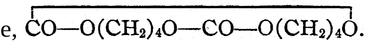
The residue was purified by dissolving it in chloroform and precipitating it with absolute alcohol while cold. The oily precipitate soon crystallized to a cream-colored powder; weight 6.3 g. or 54% of the calculated; m. p. 55–59°; very soluble in cold benzene, chloroform, acetone, and acetic acid; insoluble in ether, alcohol and petroleum ether. It gave a sharp x-ray diffraction pattern. Before analysis it was dried for four days at 80° in high vacuum. For analytical data see Table I.

Di-*p*-nitrobenzoate of Tetramethylene Glycol.—Prepared from the glycol and the acid chloride in pyridine; crystallized from boiling acetic acid; m. p. 175°.

Anal. Calcd. for $C_{18}H_{16}O_8N_2$: C, 55.67; H, 4.12. Found: C, 56.19, 56.00; H, 4.31, 4.14.

Thermal Decomposition of Tetramethylene Carbonate.—An attempt was made to bring about the depolymerization of tetramethylene carbonate by heating it to high temperature in *vacuo*. The tetramethylene carbonate was prepared from 9.0 g. of glycol and 11.8 g. of ethyl carbonate in the same manner as described above. It was heated at 0.9 mm. in a small Claisen flask by means of a metal-bath. Very slight distillation occurred as the temperature of the bath was raised from 270 to 300°. Between 300 and 325° evolution of gas occurred and the pressure increased. From the distillate were isolated 0.1 g. of crystalline solid and 2.8 g. of oil. The residue remaining in the distilling flask weighed 3 g. and was apparently identical with the polymeric tetramethylene carbonate described above; it melted at 55° and had the same physical appearance and solubility behavior.

The crystalline distillate separated from alcohol in minute prisms melting at 175–176°. Analysis and molecular weight determinations showed it to be dimeric tetramethylene carbonate,



$CO—O(CH_2)_4O—CO—O(CH_2)_4O$.

Anal. Calcd. for $(C_5H_8O_3)_2$: C, 51.71; H, 6.94; mol. wt., 232. Found: C, 51.77; 51.80; H, 6.95; 7.02; mol. wt., in boiling ethylene chloride, 194,231; mol. wt., in freezing benzene, 204.

The liquid distillate had a pungent mint-like odor and readily absorbed bromine in acetic acid solution. It is a mixture and no chemical individuals have as yet been isolated from it.

Pentamethylene Carbonate.—This was prepared from 5.9 g. of ethyl carbonate and 5.2 *g*. of pentamethylene glycol to which a small amount of sodium had been added. The mixture was heated for twelve hours at 120–160°; 76% of the calculated amount of alcohol was found in the distillate. The residue after it had been freed from sodium was heated at 250° under 0.15 mm. The distillate (1.1 g.) boiled at 110–130" and consisted chiefly of unchanged glycol; di-$-nitrobenzoate, m. p., 104–105°. The non-volatile sirupy residue crystallized on standing to a hard waxy material; weight, 4.1 g. or 63% of the theoretical. It was purified by precipitation with absolute alcohol from a cold chloroform solution as a granular and slightly colored powder; m. p., 44–46°; very soluble in benzene, chloroform, acetone and acetic acid; insoluble in ether, alcohol and petroleum ether. Before analysis it was dried to constant weight in high *vacuo*. For analysis see Table I.

Di-p-nitrobenzoate of Pentamethylene Glycol.—From the glycol and the acid chloride in pyridine; crystallized from a mixture of benzene and alcohol; m. p., 104–105°.

Anal. Calcd. for $C_{19}H_{18}O_8N_2$: C, 56.71; H, 4.51. Found: C, 56.95, 57.02; H, 4.59, 4.69.

Hexamethylene Carbonate.—This was prepared from 12 *g*. of ethyl carbonate and 12 g, of hexamethylene glycol to which a small piece of sodium had been added. The mixture was heated from 130 to 170° during two hours; 86% of the calculated amount of alcohol was found in the distillate. The residue after the removal of the sodium was subjected to distillation in high vacuum. A very small amount of distillate was found to consist of unchanged glycol. The residue, which amounted to 10 g. or 67% of the calculated, solidified on cooling to a light colored, horny, tough mass. It was soluble in benzene, acetone and chloroform; insoluble in ether and alcohol; m. p. 55–60°. A sharply defined x-ray diffraction pattern (Fig. 3) showed it to be crystalline. For analysis see Table I.

Dicarbethoxyhexane.—In an experiment similar to the above, ethyl carbonate and glycol were used in the ratio of 2 moles to 1 (24 *g*. of ester and 12 *g*. of glycol). The calculated amount (9.2 g.) of alcohol was collected. The residue after removal of sodium was subjected to vacuum distillation. It yielded 5.5 g. of distillate, b. p. 130–140° at 0.8 mm. The residue could not be distilled, and neither the distillate nor the residue could be induced to crystallize. No ethyl carbonate was found in the distillate. The distillate was dicarbethoxyhexane; n_D^{20} 1.4310; d_{20}^{20} 1.065; d_{20}^{25} 1.056.

Anal. Calcd. for $C_{12}H_{22}O_6$: C, 54.94; H, 8.41; mol. wt., 262. Pound: C, 55.00; H, 8.41; mol. wt. in boiling benzene, 236,240,245.

The oily residue was very soluble in alcohol and ether. Its analytical composition corresponded with the formula $C_2H_5O—CO—O(CH_2)_6O—CO—O(CH_2)_6O—CO—O(CH_2)_6O—CO—OC_2H_5$.

And. Calcd. for $C_{26}H_{46}O_{12}$: C, 56.73; H, 8.36; CO_2 on hydrolysis, 33.1%; mol. wt., 532. Found: C, 56.77, 57.00; *H,* 8.41, 8.53; CO_2, 34.15; mol. wt. in boiling benzene, 573, 549, 528. The CO_2 was determined by saponifying with alcoholic sodium hydroxide and weighing the sodium carbonate formed.

Carbonate of **Diethylene** Glycol.—This was prepared in 43% yield by the method used in the preparation of the other carbonates. It was a light colored sirup which could not be induced to crystallize; insoluble in alcohol and ether, quite soluble in acetone and benzene, very soluble in chloroform and hot ethyl acetate. On standing it appeared to decompose to some extent into acetaldehyde and carbon dioxide and for this season it could not be dried to constant weight. For analysis see Table I.

Decamethylene Carbonate.—This was prepared in 75% yield by the method used for the preparation of the other carbonates. It was soluble in benzene and chloroform but insoluble in alcohol. It was purified by precipitation from chloroform with alcohol in the cold. The oily product gradually solidified to a cream-colored powder; m. p. 55°; very soluble in chloroform, slightly soluble in ether, benzene, acetone and acetic acid; insoluble in alcohol and petroleum ether. This powder gave a sharply defined x-ray diffraction pattern. Before analysis it was dried to constant weight in high vacuum at 90°. For analysis see Table I.

p-**Xylylene** Carbonate.—This was prepared from *p*-xylylene glycol and ethyl carbonate as in the preparation of the other carbonates. The residue after completion of the ester interchange was insoluble in hot benzene, absolute alcohol, chloroform and carbon tetrachloride; slightly soluble in acetic acid. It dissolved more or less completely in ethylene chloride, anisole and dioxane. It was thoroughly triturated with water and with cold alcohol to remove sodium and excess glycol and ethyl carbonate. The amount of the white solid remaining corresponded to 82% of the calculated. It was separated into two fractions by extraction with ethylene chloride.

(a) Soluble Fraction.—This was precipitated with ether from ethylene chloride in the form of white flocks; m. p. 137–138°. For analysis see Table I.

(b) Fraction Insoluble in Ethylene Chloride.—This was insoluble in the common organic solvents; m. p. 177–185° (rather indefinite). For analysis see Table I.

Attempted Preparation of Methylene Carbonate.—Silver carbonate (81 g.) was heated with methylene bromide (51 g.) in dry toluene solution. Formaldehyde and carbon dioxide were formed and free silver was produced. From the reaction mixture there was isolated only a small amount of oil with a sweet odor—probably methylene carbonate. This liberated formaldehyde on heating: $CH_2CO_3 \longrightarrow H_2CO + CO_2$.

We are indebted to Dr. A. W. Kenney and Mr. Henry Aughey for the x-ray diffraction pictures, to Mr. W. H. Taylor for many molecular-weight determinations and to Mr. G. A. Jones for determinations of carbon and hydrogen.

Summary

The following compounds have been prepared by the action of the appropriate glycols on ethyl carbonate: trimethylene carbonate, tetramethylene carbonate, pentamethylene carbonate, hexamethylene carbonate, decamethylene carbonate, diethylene carbonate and p-xylylene carbonate. Their properties are described. In accordance with a generalization already set forth, ethylene carbonate and trimethylene carbonate are monomeric and the other carbonates are polymeric. Trimethylene carbonate undergoes reversible A polymerization. A stable dimeric form. of tetra-

methylene carbonate has been prepared by thermal decomposition of its usual polymeric form. Hexamethylene carbonate is tough and elastic.

WILMINGTON, DELAWARE

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

STUDIES OF CONJUGATED SYSTEMS
II. THE BROMINATION OF VINYLACRYLIC ACID

BY IRVING E. MUSKAT, BRUNNER C. BECKER AND JOEL S. LOWENSTEIN

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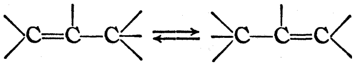
The abnormal addition reactions of conjugated systems have been the subject of a great deal of experimental work ever since Fittig[1] and Baeyer[2] found that compounds containing two double bonds in conjugation were reduced in the 1,4- rather than in the 1,2- or 3,4-positions, and did not exhibit the properties common to ordinary ethylenic double bonds. In 1899 Thiele[3] proposed his "partial valence" theory to interpret these 1,4-addition reactions to conjugated systems and brought a great deal of experimental evidence in its favor. According to this theory the type of addition taking place in a conjugated system depends solely on the valence relations of that system. Later work[4] proved this general theory to be incorrect, and it was modified by Hinrichsen[4] to take into consideration the electrochemical nature of the entering atoms or groups, as well as the nature of the original unsaturated compound in which the addition is taking place, More recent work,[5] carried out with greater precision and more refined technique, has shown that in many addition reactions where 1,4-addition is found, it is not due primarily to 1,4-addition but rather to an isomerization of the 1,2- or 3,4-addition compounds. Such isomerizations are common in three-carbon systems containing a double bond



Because of the theoretical importance of the addition reactions of conjugated systems, it was considered desirable to make a thorough investigation of such addition processes, particularly in simple conjugated systems. It was hoped that such studies would also throw some light on the mecha-

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[1] Fittig, *Ann.*, 227, 46 (1888).

[2] Baeyer, *ibid.*, 251, 271 (1889); 256, 1 (1890).

[3] Thiele, *ibid.*, 306, 87 (1899).

[4] Michael, *J. prakt. Chem.*, 60, 467 (1899); Erlenmeyer, Jr., *Ann.*, 316, 43 (1901); Vorlander, *Ber.*, 36, 2339 (1903); Kohler, *Am. Chem. J.*, 31, 642 (1904); 33, 153, 333 (1905); Hinrichsen, *Ann.*, 336, 174 (1904); Strauss, *Ber.*, 42, 2866 (1909); Ingold, *J. Chem. Soc.*, 121, 329, 1306 (1921); and many others.

[5] Ingold and Shoppee, *J. Chem. Soc.*, 129, 1477 (1926); Farmer, *ibid.*, 172 (1929); Prevost, *Ann. chim.*, [10] 10, 113 (1928); Claisen, *J. prakt. Chem.*, 105, 65 (1922).

nism of addition reactions and directive influence in the aromatic series. The present paper, the second of the series, contains the results of an investigation on the bromination of vinylacrylic acid.

Thiele[6] proved that vinylacrylic acid adds hydrogen in the 1,4 (or 1,6)-position. Kohler and Butler,[7] while studying the relative ease of 1,4- and 1,6-addition, showed that sodium malonic ester combines with the esters of vinylacrylic and sorbic acids to give 1,6-addition products, while phenylmagnesium bromide reacts with the same esters to give first the corresponding ketones, which react further to give 1,4-addition products.

In a recent publication by Farmer and Healy[8] on "Addition to Butadiene Esters," the authors also report the bromination of vinylacrylic acid. They found that bromine adds to vinylacrylic acid in the 3,4-position to give a liquid dibromide from which they were able to separate a solid dibromide melting at 47°. They treated the dibromide with diethylamine and obtained a monobromide which polymerized so rapidly that they were unable to determine its structure or even its melting point. Quite independent of this work we have studied the bromination of vinylacrylic acid but have carried the work much further and proved the structures of our products.

Vinylacrylic acid was prepared according to a modification of Nottbohm's[9] method. The pure acid melted at 72°, the same melting point reported by Nottbohm. Doebner,[10] using a somewhat different method, had previously prepared vinylacrylic acid, reporting its melting point as 80°. Auwers[11] and Kohler[7] repeated the preparation of vinylacrylic acid: the former used Nottbohm's method while the latter used Doebner's method; both reported its melting point as 72°. Recently Farmer[8] reported the preparation of vinylacrylic acid according to Doebner's method, confirming his melting point as 80°. We prepared vinylacrylic acid according to both methods. Both preparations melted at 72° as did a mixture of the two. It is possible that there are two vinylacrylic acids which are either physical or geometric isomers of each other.

The bromination of vinylacrylic acid was then studied. It was found that vinylacrylic acid absorbed two atoms of bromine to give a dibromide which distilled at 156° under 3-mm. pressure. On standing it partially solidified to a solid melting at 47°. Farmer[8] apparently obtained the same dibromide (but does not give its boiling point) starting with the vinylacrylic acid melting at 80°. He proved its structure, 3,4-dibromo-Δ^1-pentenic

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[6] Thiele, *Ber.*, 35, 2320 (1902); see also Doebner, *ibid.*, 35, 1136 (1902).

[7] Kohler and Butler, THIS JOURNAL, 48, 1036 (1926).

[8] Farmer and Healy, *J. Chem. Soc.*, 130, 1060 (1927).

[9] Nottbohm, *Ann.*, 412, 49 (1916).

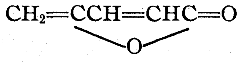
[10] Doebner, *Ber.*, 35, 1136 (1902).

[11] Auwers, *Ann.*, 432, 46 (1923).

acid, by ozonization. We confirmed his structure in every particular. Thus we see that vinylacrylic acid adds bromine in the 3,4-position and not in the 1,4-position as postulated by Thiele. This stands in variance with the hydrogenation of vinylacrylic acid, which takes place in the 1,4-position.[6]

Vinylacrylic acid dibromide readily absorbed two atoms of bromine to give the tetrabromide. It melted at 156° and was identical with the tetrabromide described by Nottbohm.[9] The vinylacrylic acid dibromide was reduced with zinc dust to give the original vinylacrylic acid melting at 72°.

On distilling the dibromide under reduced pressure, decomposition occurred with the liberation of hydrogen bromide. A lower-boiling fraction distilled over and solidified partially on standing. The solid was removed; it melted at 143° and solidified again at 162°. Its structure was finally proved by converting it into aceto-acrylic acid. This, with its analysis ($C_5H_4O_2$), showed that it was a γ-lactone having the structure

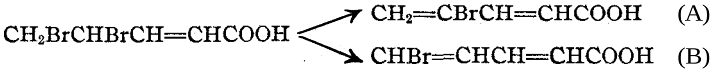


$CH_2{=}CCH{=}CHC{=}O$ (O bridging)

When vinylacrylic acid dibromide was treated with two molar equivalents of sodium hydroxide, the temperature being kept at about zero degrees, the soluble sodium salt of monobromo-vinylacrylic acid was formed in almost theoretical yield. The free acid was obtained by acidifying the alkaline solution with cold dilute acids.

Bromovinylacrylic acid is a white crystalline compound, very soluble in all ordinary organic solvents and very unstable. It readily polymerizes to a white solid which is insoluble in all ordinary organic solvents with the exception of acetone. Due to its ease of polymerization it was not possible to obtain a sharp melting point. It melted at about 106°.

It may be seen readily from the structure of the vinylacrylic acid dibromide that hydrogen bromide may be eliminated in either of two ways



$CH_2BrCHBrCH{=}CHCOOH \rightarrow CH_2{=}CBrCH{=}CHCOOH$ (A)

$CH_2BrCHBrCH{=}CHCOOH \rightarrow CHBr{=}CHCH{=}CHCOOH$ (B)

The structure of the monobromide was proved by further brominating it to the bromovinylacrylic acid dibromide and studying the oxidation products of the tribromide formed.

Bromovinylacrylic acid readily absorbed a molecule of bromine to give a tribromo derivative boiling at about 172° under 10-mm. pressure. There are six tribromides theoretically possible depending on the A or B structure of the monobromide and the 1,2-, 1,4- or 3,4-type of addition taking place

(A) $CH_2{=}CBrCH{=}CHCOOH$	(B) $CHBr{=}CHCH{=}CHCOOH$
(1–2) $CH_2{=}CBrCHBrCHBrCOOH$	(1–2) $CHBr{=}CHCHBrCHBrCOOH$
(1–4) $CH_2BrCBr{=}CHCHBrCOOH$	(1–4) $CHBr_2CH{=}CHCHBrCOOH$
(34) $CH_2BrCBr_2CH{=}CHCOOH$	(34) $CHBr_2CHBrCH{=}CHCOOH$

The bromovinylacrylic acid dibromide was ozonized in the usual manner. It was possible to recover oxalic acid (40% yield), which was identified by its melting point and a melting point of a mixture with a sample of known origin; and also α,α,β-tribromopropionic aldehyde, which was identified by the melting point of the α,α,β-tribromopropionic aldehyde hydrate and a melting point of a mixture with the synthesized product. This proves that 3,4-addition of bromine had again taken place, giving rise to a tribromide of structure $CH_2BrCBr_2CH{=\!=}CHCOOH$, and therefore the structure of the monobromide must be as represented by **(A).**

The experimental results recorded here lend support to the Hinrichsen view of addition to conjugated systems as contrasted to the Thiele view; that is, the mode of addition to conjugated systems is a function not only of the conjugated system itself, but also of the nature of the addendum.

Experimental Part

The Preparation of Vinylacrylic Acid.—The method of preparation described here is a modification of Nottbohm's[9] method. Nottbohm's method gives 15–20% of pure acid, while the Kohler[7] modiication of Doebner's method gives 30% of pure acid. The following method gave about 55–65% of pure acid.

To a solution of 118 g. of potassium metabisulfite in about 200 cc. of water, cooled in a freezing mixture, 29 g. of acrolein was added, drop by drop, under continuous stirring. After all of the acrolein had been added, the stirring was continued for two hours at room temperature. Malonic acid (52 g.) was then added and the solution was refluxed for two hours. The solution was then concentrated to a thick, sirupy mass on the water-bath until the evolution of carbon dioxide gas had ceased. During this time the viscous mass was stirred in order to avoid excessive frothing. The residue was then dissolved in about 100 cc. of water, which is contained in an iron dish, and 300 g. of coarsely ground sodium hydroxide was gradually added with continuous stirring. It was then heated on the water-bath for four hours, after which it was allowed to cool. The semi-crystallized mass was placed in a large enamel dish to which was added about 500 g. of ice and 500 g. of chloroform. The mixture was then slowly neutralized with 25% hydrochloric acid under continuous stirring. During the neutralization ice was added to keep the temperature at about zero degrees. The chloroform layer was separated and the acidic layer was twice extracted with chloroform. The chloroform extract was dried and the chloroform removed under reduced pressure. The yellow residue (about 40 g.) was recrystallized from ligroin. The pure acid (about 30 *g.)* melted sharply at 72°.

Vinylacrylic acid was also prepared according to Doebner's method[10] by the direct condensation of acrolein and malonic acid in the presence of pyridine. The purified acid thus prepared also melted at 72°, as did a mixture of the acids prepared by each method.

Vinylacrylic Acid Dibromide.—Vinylacrylic acid dibromide was prepared by the addition of the theoretical amount of bromine dissolved in chloroform to a solution of vinylacrylic acid in chloroform. Absorption took place fairly readily and the reaction mixture became warm. The reaction mixture was distilled under reduced pressure; a light yellow oil distilled over at 156° under 3 mm. pressure. On standing it partially crystallized to a solid melting at 47°, which is the same melting point recorded by Farmer for his dibromide, which he obtained from vinylacrylic acid melting at 80°.

Anal. Calcd. for $C_5H_6O_2Br_2$: Br, 61.98. Found: Br, 61.91, 62.01.

The conditions under which the vinylacrylic acid was brominated were varied considerably. Various solvents such as ligroin, carbon tetrachloride, carbon bisulfide and glacial acetic acid were used besides chloroform, and the temperature was varied from about −20° to about 50°. However, in all cases only one dibromide was obtained, regardless of the experimental conditions employed. The dibromide is unstable, particularly toward heat and alkali, and loses hydrogen bromide easily.

The pure vinylacrylic acid dibromide (4.2 g.), dissolved in chloroform, was subjected to ozonization and the ozonide thus formed was decomposed with water. To assure the complete decomposition of the ozonide it was warmed on the water-bath for a short time. The mixture consisted of aldehydes and acids and was separated by extracting the aqueous solution several times with ether. The aqueous solution was carefully evaporated to dryness and further heated in the oven to 110° for several hours. The residue (1.10 g.) melted at 187°, the melting point of anhydrous oxalic acid. A mixture with pure oxalic acid also melted at 187°. This corresponds to a 75% yield of oxalic acid. The aldehyde portion was distilled under reduced pressure. An oil distilled over at 80° under 5–6 mm. pressure, the boiling point of α,β-dibromopropionic aldehyde. This was further identified by treating with sodium acetate according to the method of Piloty and Stock,[12] which converted the dibromide into a-bromo-acrolein. This distilled over at 49–50° under 30 mm. pressure, the recorded boiling point of α-bromo-acrolein. The a-bromo-acrolein gave a semicarbazone melting at 160° with decomposition. This proves beyond any doubt that bromine had added to vinylacrylic acid in the 3,4-position.

Vinylacrylic acid dibromide readily absorbed two atoms of bromine to give the tetrabromide. It melted at 156° and was identical with the tetrabromide described by Nottbohrn. The dibromide was reduced with zinc dust to the original vinylacrylic acid, which was identified by its melting point. 72°. The yield was low, due to the polymerization of the vinylacrylic acid.

If vinylacrylic acid dibromide was distilled under reduced pressure, a great deal of decomposition occurred at about 140° with the liberation of hydrogen bromide. A lower-boiling fraction distilled over which solidified on standing. The solid is characterized by a marked insolubility in ether and could thus be freed easily from impurities by washing with ether. It is insoluble in all ordinary organic solvents with the exception of acetone, from which it can be recrystallized in pure white crystals. It melts at 143° and solidifies again at 162°, which may indicate that polymerization has occurred. It contained no halogen and dissolved slowly in alkali to give a reddish colored solution.

Anal. Calcd. for $C_5H_4O_2$: C, 62.5; H, 4.2. Found: C, 62.6, 62.6; H, 4.4, 4.4.

The molecular weight was determined by the boiling point method in acetone, which was erratic under the conditions of the experiment. Subs., 0.3134 g.; acetone, 100 g.; *AT*, 0.063°. Calcd. for $C_5H_4O_2$: mol. wt., 96. Found: mol. wt., 86.

The titer value of the substance was then determined by dissolving it in pure acetone, diluting with water, and titrating in the usual manner with standard alkali. Subs., 0.1003: 9.8 cc. of 0.1063 *N* sodium hydroxide. Calcd. for $C_5H_4O_2$: mol. wt., 96. Found: mol. wt., 96.3.

This proved that the substance contained one carboxyl group, but its slow solubility in alkali indicated that it was a lactone. From the fact that it was formed as a result of the elimination of two molecules of hydrogen bromide from vinylacrylic acid dibromide, it is at once clear that it could be either a 6- or a γ-lactone. The 8-lactone is known. It melts at 5° and has entirely different properties from those shown by our

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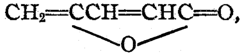
[12] Piloty and Stock, *Ber.*, 31, 1385 (1898).

compound. It was proved to be the γ-lactone,  $CH_2{=}CCH{=}CHC{=}O$ (bridged by O), by hydrolyzing it with alkali to the corresponding aceto-acrylic acid. The hydrazone of aceto-acrylic acid melts at 160° with decomposition; the hydrolysis product of our lactone also formed a hydrazone melting at 160° with decomposition. The isolation and proof of the structure of this lactone stand in good agreement with the proof of the structure of the monobromide that follows.

Bromovinylacrylic Acid.—When vinylacrylic acid dibromide was treated with one molar equivalent of aqueous sodium hydroxide, the soluble sodium salt of the dibromide was formed. If another molar equivalent of sodium hydroxide was added, the temperature being kept at about 0° during this operation, the dibromide easily lost a molecule of hydrogen bromide and was thus converted into the soluble sodium salt of the monobromovinylacrylic acid, with an almost theoretical yield. It is of the utmost importance to keep the temperature very low, otherwise the monobromide polymerizes. The free acid was precipitated as a voluminous crystalline mass by acidifying the alkaline solution with cold dilute acids.

Anal. Calcd. for $C_5H_5O_2Br$: Br, 45.16. Found: Br, 45.07, 45.15.

The bromovinylacrylic acid is a white, crystalline compound, very soluble in the ordinary organic solvents and very unstable. It readily polymerizes to a white solid which is insoluble in all ordinary organic solvents with the exception of acetone. Due to its ease of polymerization it was not possible to obtain a sharp melting point. It melted at about 106°. The structure of the monobromide was established by further brominating it to the bromovinylacrylic acid dibromide and determining the oxidation products of the tribromide formed.

Bromovinylacrylic Acid Dibromide.—Bromovinylacrylic acid dibromide was prepared by the addition of the theoretical amount of bromine dissolved in chloroform to a solution of bromovinylacrylic acid dissolved in chloroform. Absorption took place fairly readily and the mixture became warm. The reaction mixture was distilled under reduced pressure. A light yellow oil distilled over at about 172" under 10 mm. pressure.

Anal. Calcd. for $C_5H_5O_2Br_3$: Br, 71.19. Found: Br, 71.23, 70.58.

The pure bromovinylacrylic acid dibromide (1.1 g.) was subjected to ozonization and the ozonide thus formed was worked up in the manner previously described for the vinylacrylic acid dibromide. The acid and aldehyde portions were separated; the acid portion yielded 0.17 g. of calcium oxalate, which corresponds to a 40% yield, while the aldehyde was removed as such and distilled under reduced pressure. It distilled over at 104–106° under 30-mm. pressure, the boiling point of α,α,β-tribromopropionic aldehyde. We completely verified the α,α,β-structure of the tribromopropionic aldehyde by preparing the hydrate, which melted at 57° and did not lower the melting point of the synthesized α,α,β-tribromopropionic aldehyde hydrate when mixed with it. This proves that the brornovinylacrylic acid dibromide has the structure $CH_2BrCBr_2CH{=}CH$-COOH, and consequently the bromovinylacrylic acid has the structure $CH_2{=}CBr$-$CH{=}CHCOOH$.

Summary

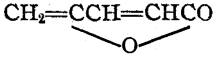
1. By bromination of vinylacrylic acid a dibromide is formed whose structure was proved by ozonization to be a 3,4-derivative, rather than a 1,4-derivative as required by Thiele's theory of addition to conjugated systems.

2. 3,4-Dibromo-Δ^1-pentenic acid loses a molecule of hydrogen bromide to give 3-bromovinylacrylic acid.

3. 3-Bromovinylacrylic acid absorbs one molecule of bromine in the 3,4-position to give 3,3′,4-tribromo-A^1-pentenic acid. Its structure was proved by ozonization.

4. An improved method for the preparation of vinylacrylic acid is given which doubles the best yield heretofore obtained.

5. On distillation 3,4-dibromo-Δ^1-pentenic acid loses two molecules of hydrogen bromide to give a γ-lactone whose structure was proved to be



$$\underset{\diagdown O \diagup}{\mathrm{CH_2{=}CCH{=}CHCO}}$$

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

CARBITHIOIC ACID STUDIES. I. TOLYL-4-CARBITHIOIC ACID AND CERTAIN DERIVATIVES[1]

BY R. W. BOST AND W. J. MATTOX

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There are three methods by which the carbithioic acids are usually made, namely, hydrolysis of the corresponding thio esters with alcoholic potassium hydroxide,[2] the action of carbon disulfide on benzene in the presence of anhydrous aluminum chloride[3] and the Grignard reaction.[4,5]

Sakurada[2] first isolated tolyl-4-carbithioic acid by the hydrolysis of ethyl dithio-p-toluate with alcoholic potassium hydroxide, the ethyl dithio-p-toluate being prepared by passing dry hydrogen sulfide into an ethereal solution of the corresponding thio-imino ester. However, none of its properties was studied and no derivatives were prepared other than the ethyl ester.

In this paper is described the preparation of tolyl-4-carbithioic acid by the action of carbon disulfide on tolyl-4-magnesium bromide. The acid is a viscous red oil having a disagreeable odor. Attempts to distil the acid resulted in decomposition. The sodium salt was more stable and was used in the preparation of the derivatives

Tolyl-4-carbithioic acid readily forms salts with the chlorides and acetates of inorganic metals. It is easily converted into thio esters by alkyl sulfates and alkyl halides. The thio esters are susceptible to ammonolysis, whereupon thio amides are obtained. In these respects the —CSSH group is similar to the —COOH group.

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[1] This paper is an abstract of a thesis submitted in June, 1929, to the Faculty of the University of North Carolina by W. J. Mattox in candidacy for the degree of Master of Arts.

[2] Sakurada, Mem. *Coll. Sci.* Kyoto, 10, 79-83 (1926).

[3] Jorg, Ber.,60, 1466 (1927).

[4] Houben, *ibid.*, 39, 3219 (1906).

[5] Wheeler and Thomas, THIS JOURNAL, 50,3106 (1928).

The acid differs from the carboxylic acids in that the —CSSH group is converted by oxidizing agents such as nitric acid and permanganate into the —COOH group. Attempts to prepare an acid chloride were negative.

Experimental Part

Tolyl-4-magnesium Bromide.—Thirteen grams of clean, dry magnesium shavings was placed in a liter balloon flask provided with a reflux condenser and a mixture of 200 ml. of absolute ether and **25** g. of *p*-bromotoluene added. A small crystal of iodine was allowed to dissolve on the bottom. The reaction usually started in a few minutes. p-Bromotoluene was then added in 10-ml. portions until **85** g. had been added. After the reaction was complete, the ether solution was decanted into a dry flask.

Tolyl-4-carbithioic Acid.—The flask containing the Grignard reagent was surrounded by a freezing mixture and cooled to 0°; **38** g. of carbon disulfide was added dropwise so that the temperature did not rise above 0°. This required about an hour. Precautions were taken to exclude all moisture. After all of the carbon disulfide had been added the stirring was continued for about three hours. The ice-bath was removed and the reaction product allowed to stand at room temperature for an hour or longer. The solution was poured into 500 g. of ice and dilute hydrochloric acid then added to dissolve the magnesium hydroxide. The deep red ether layer was removed by means of a separatory funnel and extracted with 100-ml. portions of 5% sodium hydroxide until the latter was only slightly colored. This aqueous solution of the sodium salt was covered with 200 ml. of ether and dilute hydrochloric acid added until the aqueous solution was slightly acid. The free acid which was then in solution in the ether was washed well with water. From three to four precipitations from the aqueous solution of the sodium salt were necessary to purify the acid. The ether was evaporated in a desiccator to obtain the free acid.

Tolyl-4-carbithioic acid is a dark red, viscous oil having a disagreeable odor. All attempts to distil it, even at 3-mm. pressure, resulted in decomposition. It solidifies at 27° into a mass of dark red crystals. It is very soluble in benzene, toluene, ether and acetone, slightly soluble in alcohol, carbon tetrachloride and chloroform and insoluble in water. The acid decomposes slowly on exposure to the atmosphere, but is much more stable in ether solution.

Zinc Salt of Tolyl-4-carbithioic Acid.—Five grams of zinc acetate dissolved in 150 ml. of water was added to 15 ml. of acetic acid. To this solution was slowly added, with stirring, a slight excess of the sodium salt of the acid and the stirring continued for three to four hours. It is necessary to keep the sodium salt in excess as otherwise complex products are formed. After the precipitate was washed and dried, the zinc salt was twice extracted with hot absolute alcohol. It is soluble in benzene, toluene and hot alcohol.

Lead Salt of Tolyl-4-carbithioic Acid.—This salt was prepared similarly to the zinc salt. It is practically insoluble in all the organic solvents.

Methyl Ester of Tolyl-4-carbithioic Acid.—An aqeuous solution of the sodium salt was treated with dimethyl sulfate, with shaking, until a dark red oil separated out and the red color had disappeared from the aqueous layer. The mixture was gently refluxed for thirty minutes to insure complete reaction. The ester was extracted with ether, the ethereal solution washed with water, dried and distilled in vacuum. It is a dark red oil having a disagreeable odor.

Ethyl Ester.—This ester was prepared similarly to the methyl ester, using the corresponding alkyl sulfate. It resembles the methyl ester in its physical properties.

n-Butyl Ester.—Ninety-five grams of the sodium salt of the acid dissolved in 300 ml. of water and 70 g. of *n*-butyl bromide were refluxed until a red oily layer separated out and the aqueous layer was colorless. When cooled, the ester was extracted with ether, washed, dried and distilled in vacuum. It is a red oily liquid of disagreeable odor and solidifies at 20°.

p-**Nitrobenzyl** Ester.—To 4 g. of *p*-nitrobenzyl bromide dissolved in 40 ml. of hot alcohol was slowly added, with stirring, a freshly prepared aqueous solution of the sodium salt in slight excess. Gentle boiling was continued for five minutes. After cooling the dilute alcohol was decanted off the thick oil which separated out. The oil was washed with 95% alcohol and placed on a porous plate to crystallize. The crude ester was purified by dissolving in hot absolute alcohol and heating with several portions of charcoal. The filtrate upon cooling yielded large red rectangular plates in the form of clusters. The ester is soluble in ether, hot toluene, alcohol and benzene.

Amide of Tolyl-4-carbithioic Acid.—Seven grams of the methyl ester and 20 ml. of concentrated ammonium hydroxide were placed in a 50-ml. glass-stoppered bottle for five or six days. The bottle was shaken occasionally during this time. The crude amide which separated out, was filtered off, washed with petroleum ether and crystallized from hot toluene. It is soluble in ether, hot alcohol and benzene. Methyl mercaptan is also formed in the reaction.

p-Toluide of Tolyl-4-carbithioic Acid.—Ten grams of *p*-toluidine, 6 g. of the dry sodium salt and 6 ml. of concentrated hydrochloric acid were placed in a small beaker and gently heated for thirty minutes. The product was cooled and extracted with 50 ml. of hot toluene. The toluene solution was boiled with several portions of charcoal, filtered and set aside to crystallize. Long yellow needles separated out when about one-third of the toluene had evaporated. It is soluble in hot alcohol, benzene and toluene.

Oxidation of Tolyl-4-carbithioic Acid.—To an ether solution of the acid cooled to 0° was added nitric acid (sp. gr. 1.42) dropwise, with stirring, until the red color of the acid changed to a light yellow. The mixture was removed from the ice-bath and stirring continued for an hour. The oxidation product was extracted with ether, purified through its sodium salt and finally recrystallized from dilute alcohol. The white crystalline product melted at 181°. Qualitative tests for sulfur were negative. Molecular-weight determinations and other tests proved the oxidation product to be *p*-toluic acid. Similar results were obtained with potassium permanganate at room temperature. At higher temperatures complex products are obtained.

Action of Phosphorus Pentachloride on Tolyl-4-carbithioic Acid.—Phosphorus pentachloride reacts with the acid, producing a viscous red liquid. All attempts to distil the product in a vacuum resulted in decomposition. Phosphorus trichloride and phosphorus oxychloride were used and similar results obtained.

TABLE I

DATA ON DERIVATIVES

No.	*Compound*	*Color*	*Form*	Solvent	*M.* p., °C.
1	Zinc salt	Light red	Amorphous	Hot abs. alcohol	180
2	Lead salt	Brick-red	Amorphous	None	200 (decomp.)
3	Amide	Lemon-yellow	Needles	Hot toluene	155
4	Toluide	Yellow	Needles	Hot toluene	170.5
5	*p*-Nitrobenzyl ester	Red	Plates	Hot abs. alcohol	70.5
				Sp. gr., at 30°	B. p., °C.
6	Methyl ester	Red	......	....	130 (3 mm.)
7	Ethyl ester	Red	......	1.1173	132 (3 mm.)
8	n-Butyl ester	Red	......	1.0700	169 (5 mm.)

TABLE II

ANALYSES

No.	Formula	Carbon Calcd.	Carbon Obs.	Hydrogen Calcd.	Hydrogen Obs.	Sulfur Calcd.	Sulfur Obs.	Metal Calcd.	Metal Obs.
1	$C_{16}H_{14}S_4Zn$	48.03	48.08	3.53	3.66	32.08	32.14	16.36	16.22
2	$C_{16}H_{14}S_4Pb$	35.45	35.80	2.60	2.70	2368	23.94	38.26	38.18
3	C_8H_9NS	63.51	63.95	6.00	6.13	2121	21.17		
4	$C_{15}H_{15}NS$	74.62	74.73	6.26	6.37	13.29	13.39		
5	$C_{15}H_{13}O_2NS_2$	59.35	59.61	4.32	4.46	21.14	20.99		
6	$C_9H_{10}S_2$	59.27	58.75	5.53	5.65	35.19	35.14		
7	$C_{10}H_{12}S_2$	61.15	60.64	6.16	6.16	32.68	32.65		
8	$C_{12}H_{16}S_2$	64.21	63.60	7.19	7.37	28.59	28.71		

Summary

1. Tolyl-4-carbithioic acid was prepared by the action of carbon disulfide on tolyl-4-magnesium bromide.
2. The acid readily forms salts and esters.
3. A thio amide and the p-toluide were prepared.
4. The acid is very sensitive to oxidizing agents.
5. Attempts to prepare the acid chloride were negative.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE EFFECT OF HEAT UPON CROTONIC ACID

BY EVALD L. SKAU[1] AND BLAIR SAXTON

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In the course of a study of the mutual solubility relations of geometrical isomers, an unsuccessful attempt was made to prepare isocrotonic acid by a method based upon the work of Michael[2] and Schulthess and of Morrell and Hanson.[3] According to these investigators the product obtained upon heating crotonic acid or isocrotonic acid to a temperature above 100° is a binary mixture of these two acids. The latter authors made a more extensive study of the system and came to the conclusion that it afforded an example of "unstable" or "false equilibrium." Since there is considerable doubt whether such cases actually exist,[4] the system promised to be interesting from this point of view also.

Morrell and Hanson obtained their "equilibrium" values by heating a sample of each acid for successive six-hour periods at various temperatures and determining the primary freezing points of the solutions obtained at each temperature. (Their data are included in Table I.) The composition

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[1] Du Pont Fellow, 1924–1925.

[2] Michael and Schulthess, *J. prakt. Chem.*, [2] *46*, 236 (1892).

[3] Morrell and Hanson, *Chem. News*, 90, 166 (1904); *J. Chem. Soc.*, 85, 1520 (1904).

[4] See Roozeboom, "Die Heterogenen Gleichgewichte," 1918, Vol. **11**, Part 3, p. 13; Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 17.

in each case was then read from the freezing point-composition diagram of the binary system crotonic acid–isocrotonic acid (a system of the simple eutectic type) on the assumption that only these two acids were present. Their "equilibrium curves meet at 172°" at a composition corresponding to 24% isocrotonic acid and **76%** crotonic acid.[5]

On the basis of their work we proposed to prepare a quantity of isocrotonic acid for use in another investigation. By heating a sample of crotonic acid at 172° a mixture freezing at about 50" should be obtained, from which we hoped to get a 34% yield of liquid having the eutectic composition **(70%** isocrotonic acid) by filtering the crotonic acid separated just above the eutectic temperature, −3°. It seemed probable that the isocrotonic acid could be isolated from this solution since Wislicenus[6] was able to obtain it from Kahlbaum "Isocrotonic acid" which was found by him to be only **33%** pure.

Upon carrying out this procedure, the heating being at various temperatures ranging from 125 to 175°, a liquid was obtained by filtering at 0° which did not solidify completely at −3°, nor could isocrotonic acid be isolated from it by Wislicenus' method.

A study of the equilibrium mixtures showed that they are not simple binary but at least ternary mixtures containing crotonic acid, probably some isocrotonic acid and a third substance which has been isolated in 90–95% purity. The evidence seems to show that this third substance is a double molecule having one free carboxyl group and one double bond, the suggested formula being $CH_3CH{=}CHCOOCH(CH_3)CH_2COOH$.

It has also been shown that above **110"** the system does not exhibit the phenomenon of "false equilibrium" as Morrell and Hanson stated.

Effect of Heating Upon Certain Properties of Crotonic Acid

Materials.—The first part of the work was carried out on a sample of Kahlbaum crotonic acid obtained through the courtesy of the Bureau of Chemistry; later, samples were purchased from the Sylco Laboratories of Chicago. In all cases the acid was repeatedly crystallized from petroleum ether, the purified product giving a flat on its time–temperature curve at 71.4°.[7] Successive vacuum sublimation also proved to be an effective method of purification.

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[5] They suggested the possibility of compound formation within the range 138–145° inasmuch as the sample of isocrotonic acids after being heated at 145° failed to solidify completely at −19°, whereas the eutectic temperature for the crotonic–isocrotonic acid system is −3° as determined by themselves. They state that with the possible exception of this temperature range, preliminary experiments on the equilibrium in the liquid phase seemed to indicate the absence of compound formation below 170".

[6] Wislicenus, *Vierteljahrsschrift der naturforschenden gesellschaft in Zurich*, **41**, *270* (1896); *Verh. d. Vers. deutsch. Ntf. u. Arzte*, (II) **1**, 78 (1895).

[7] It may be noted that this is 0.5° below the value given by Morrell and Hanson. On the basis of purity of material and accuracy of temperature measurement, we believe our value to be the more accurate. By means of heat content curves, Lynn, in this Laboratory, estimated that the impurity was less than 0.03 mole per cent.

Method of Heating.—Samples sealed in evacuated tubes were heated at different temperatures between 97 and 170° for various periods of time. The resulting mixtures, in some cases after the crotonic acid which separated on cooling had been removed by filtration, were examined with reference to the following properties.

Freezing Point.—The apparatus used has already been described.[8] Since it is difficult to control the supercooling of crotonic acid mixtures, it was impossible to use Andrews, Kohman and Johnston's[9] method of correction for the amount of solvent which separated. Instead, the surroundings (the copper shield) were set at various temperatures below the freezing point and the highest maximum after crystallization was taken as the freezing point. The values are, therefore, accurate for pure crotonic acid and the error increases with the increase in concentration of the other components up to probably 1.5' for the most concentrated solutions.[10]

We confirm the finding of Morrell and Hanson that the freezing point is lowered by previous heating and our results show fairly good agreement with theirs for equal periods of heating (see Table I). That these are not the equilibrium values at the respective temperatures, as these investigators evidently assumed, is shown by the fact that further heating at the same temperature caused additional lowering, as can be seen from this table. In fact, by heating a sample of crotonic acid for 165 days at 110° (±1°), a freezing point of 41° was attained, a value which was decidedly lower than any of theirs, even though in some cases they heated to 168°.

TABLE I

THE CHANGE IN FREEZING POINT UPON HEATING THE CROTONIC ACIDS

Morrell and Hanson				Skau and Saxton		
Duration of heating,* hours	Temp. of heating, °C.	Freezing point, Tube I (isocrotonic). °C.	Freezing point. Tube II (crotonic), °C.	Heating, hours	Temp. of heating (±1°), °C.	Freezing point, (crotonic), °C.
0	...	14.96	71.96	0	...	71.4
6	100	13.6	70.5	6	100	70.8
6[a] more	126	10.8	68.4	6.5 more	125	68.7
6 more	138	3.1	64.8	10 more	127	66.9
6 more	145	–3.1	60.3	56 more	123	*52*
6 more	152	21	55.8			
6[a] more	160	37.6	52.8			
6[a] more	168	46	51			

[a] The time of heating is not specifically stated, but it is to be implied that each period was six hours.

Acid Value and Bromination Value.—The acid value is taken as the number of grams of crotonic acid equivalent to the amount of standard alkali used per gram of sample. It was determined by direct titration in dilute alcohol solution using phenolphthalein as an indicator. The bromination value is taken as the number of grams of crotonic acid equivalent to the amount of bromine absorbed by one gram of sample. It was obtained by the method of Gaebel,[11] extending the time for absorption to exactly four hours.

The acid value and the bromination value were always numerically equal within

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[8] Skau and Saxton, THIS JOURNAL, 50, 2693 (1928).

[9] Andrews, Kohman and Johnston, *J. Phys. Chem.*, *29*, 914 (1925).

[10] For a discussion of the error due to this procedure see Andrews, Kohman and Johnston, Ref. **9**.

[11] Gaebel, *Arch. Pharm.*, 250, *72* (1912).

experimental accuracy and were always less than unity. For example, sixty-five hours at 110° gave 0.934; one hundred and twenty hours at 127° gave 0.816; and seven hours at 175° gave 0.891. Since the values for crotonic acid and isocrotonic acid are both unity, these results prove that there is some other substance or substances present in the heated product.

Saponification Value.—This seems to be unchanged by previous heating.

The Reversibility of the Reaction.—To test whether we were dealing with a case of true equilibrium, the final state was approached from two sides in the following manner. A sample of crotonic acid was heated at 160° for thirty-five hours and, after cooling to room temperature, the solid crotonic acid was removed by filtration. The remaining liquid gave a primary freezing point of 18.9° and an acid value of 0.750. Samples of this liquid, "Mixture I," and of pure crotonic acid were sealed in separate evacuated tubes and heated at constant temperature for a number of months. Their freezing points and acid values were then determined, as recorded in Table II.

TABLE II

EQUILIBRIUM VALUES REACHED FROM OPPOSITE SIDES

No.	Sample	Original freezing point, °C.	Duration of heating, months	Temp. of heating (*1°), °C.	Freezing point, °C.	Acid value
I	Crotonic	71.4	5.5	110	41.8	0.710
II	"Mixture I"	18.9	5.5	110	41.0	.703
III	Crotonic	71.4	6.5	125	48.2	.816[a]
IV	"Mixture I"	18.9	6.5	125	45.9	.772
V	"Mixture I"	18.9	5.0	(Room temp.)	19.1	.750

[a] Slight decomposition took place in this tube as was evidenced by the development of considerable pressure.

Besides indicating that above 110° we are dealing with a true and not a "false" equilibrium, these results afford evidence as to the effect of temperature on the equilibrium. This will be discussed more fully below. It should also be noted that while "Mixture I" showed substantially no change at room temperature during five months, heating at 110 and at 125° caused the freezing point to rise in both cases, whereas the acid value rose in one case and fell in the other. This points to the presence of at least three substances in the equilibrium mixtures.

Attempts to Isolate Isocrotonic Acid.—Michael's method was applied to a heated sample of crotonic acid from which considerable crotonic acid had been filtered at room temperature. Instead of isocrotonic acid, however, an oily liquid having an acid value of **0.608** was obtained.[12]

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[12] Michael's method for the isolation of isocrotonic acid from the Kahlbaum "Isocrotonic acid" depends on the insolubility of the sodium salts of the foreign substances in alcohol. Wislicenus modified this by evaporating the alcoholic solution to a smaller volume and then precipitating a considerable amount of the remaining impurities by adding ether. He thus got a product which was nearly solid at 0°, whereas that obtained by Michael's method contained only a small amount of solid at that temperature.

The product obtained by the use of Wislicenus' modification on a similar sample had essentially the same properties, but undoubtedly contained less crotonic acid, It was a light brown liquid, not crystallizable at −78°, and was insoluble in water but very soluble in alcohol or ether. Its acid value was 0.535 and its bromination value approximately the same, 0.525. It appeared to be very readily hydrolyzed, for, after neutralizing, more acid seemed to be formed on heating, and if titrated back to neutrality occasionally the amount of alkali used approached a total corresponding to an acid value of unity. The saponification value was unity.[13]

From the depression of the freezing point of pure crotonic acid caused by the addition of various small amounts of this liquid, its apparent molecular weight was calculated[14] to be 144; that is, its molecular complexity was 1.67 times that of crotonic acid, thus corresponding to double molecules which are dissociated into single molecules to the extent of 20%.[15]

Distillation under diminished pressure of one of the samples of heated crotonic acid confirmed our conclusion that very little isocrotonic acid was present. We obtained a low-boiling fraction having an acid and a bromination value substantially of unity; a middle fraction rich in crotonic acid and, as the largest fraction, a high-boiling liquid (165–173° at 24 mm.)[16] which had an acid value of 0.679 and a bromination value of 0.671 and from which crotonic acid separated at room temperature.

Nature of the Products Formed.—All of the above data indicate that the system contains at least three substances: (1) crotonic acid; (2) a low-boiling constituent which comes over with the crotonic acid in a vacuum distillation; and (3) a high-boiling constituent which constitutes the major portion of the product obtained on applying the Michael–Wislicenus method for isolating isocrotonic acid.

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[13] The low acid value, the high boiling point and the saponification value might be explained by the presence of an acid anhydride. To test this possibility, a sample from which the solid crotonic acid was filtered at 0° was treated in one case with a slight excess of alkali and in another with an excess of solid sodium carbonate in a small amount of water and then extracted thoroughly with ether. The ether extracts contained a slight amount of a brown resinous substance representing only a small fraction of a per cent. of the original heated mixture.

[14] From the ideal freezing point–solubility equation

$$\log N = \frac{-3100}{4.575(273.1 + 71.4)} \frac{\Delta t_F}{T_F} = -1.967 \frac{\Delta t_F}{T_F}$$

in which N is the mole fraction of crotonic acid, Δt_F the freezing point depression, T_F the freezing point of the solution on the absolute scale, 71.4 the freezing point of pure crotonic acid, and 3100 the molal heat of fusion of crotonic acid as determined by Lynn [Skau and Saxton, THIS JOURNAL, 50,2693 (1928)].

[15] From the relation $x = (2/1.67) - 1$.

[16] Wislicenus, Jr., ["Dissertation," Leipzig, 1892; *Chem.* Zentr., I, 413 (1893)] found that Kahlbaum's "Isocrotonic acid" distilled almost completely below 100° at this pressure, the impurity being essentially crotonic acid.

The low-boiling constituent is probably isocrotonic acid, for in the mixture with crotonic acid, as it was obtained, the acid and bromination values were approximately equal to unity, and, therefore, its molecular weight (within 2%) is equal to that of crotonic acid. If the low-boiling fractions are thus assumed to be binary mixtures of crotonic and isocrotonic acids, their compositions *can* be estimated from their freezing points and Morrell and Hanson's freezing point–composition diagram. By such an estimation it was found that the amount of isocrotonic acid in the original heated mixture was in the neighborhood of 7%.

The high-boiling constituent appears to be a dimolecular polymer of crotonic or isocrotonic acid or an addition compound of the two acids having one free carboxyl group and one double bond. This would require acid and bromination values of 0.5. The formula $CH_3CH{=}CHCOOCH(CH_3)CH_2COOH$ seems to agree with the properties best. This was the structure attributed by Thackrah[17] to a compound distilling at 163° (24–25 mm.) from a mixture obtained by heating crotonic acid at 190–200° for a few hours. His proof for this structure was based on the fact that the compound neutralized only one-half as much alkali as the same weight of crotonic acid, and that it was readily hydrolyzed on boiling or on heating with an excess of alkali, giving crotonic acid and β-hydroxybutyric acid salts. He also claimed that crotonic acid was formed practically quantitatively[18] by heating this product for a long time at 200°.

Thackrah came to the conclusion that the liquid condensation product cannot be prepared free from crotonic acid and his lowest neutralization value corresponds to an acid value of 0.57. We have been able, however, by taking advantage of the difference in the solubility of the sodium salts in a mixture of alcohol and ether, to obtain a product having an acid value of 0.535 and have attempted to purify it further by various methods. (1) Petrol ether extraction resulted in a lowering of the acid value of the residue but the change was relatively small. (2) By using the principle of steam distillation with benzene as the carrier, the acid value of a sample was reduced from 0.634 to 0.561, but the procedure was very slow. (3) The product obtained by the last method was heated in a vacuum distilling apparatus for about six hours at 104° and 20 mm. The residual liquid, which was now a deep brown, had an acid value of 0.455 and its saponification value was unity. Due to the smallness of the sample the determination of the bromination value was omitted. The apparent molecular weight was still less than twice that of crotonic acid, the mean value of x being 0.11. The fact that the acid value was less than 0.5 might seem to

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[17] Thackrah, "Dissertation," Leipzig, 1891. To the best of our knowledge this work has never been otherwise published, the only reference to it being in another Leipzig dissertation by Wislicenus, Jr., in 1892.

[18] This seems rather doubtful, considering his method of preparation of the compound.

indicate the presence of a trimolecular compound, but it could be equally well explained by assuming the presence of a dimolecular form having no free carboxyl groups.

Effect of Temperature on the Equilibrium.—An examination of the acid values of I to IV in Table II indicates that the percentage of double molecules in the equilibrium mixtures decreases as the temperature of heating increases. This is to be expected since polymerization is, as a rule, exothermic. We have also noted indications that the percentage of the low-boiling constituent does not change proportionately to that of the double molecule. If it did, the separation of the crotonic acid at 0° would leave a liquid of the same acid value in all instances, but this was found not to be the case.

Summary

The effect of heating crotonic acid has been investigated. It has been proved that the resulting mixture is not a binary mixture, as is stated in the literature, but contains at least three compounds: crotonic acid, a low-boiling constituent (probably isocrotonic acid) and a high-boiling liquid from the properties of which its probable structure has been deduced. It has further been proved that above 110° the system does not show the phenomenon of "false equilibrium" as was previously supposed.

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THE BROMINATION OF 2,4-DIMETHOXYCINNAMIC ACID

BY MARIE REIMER AND ELISE TOBIN

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In the study, in this Laboratory, of unsaturated a-ketonic acids, certain substituted cinnamic acids have been needed for purposes of identification. This has led to the study of the bromination products of 2,4-dimethoxycinnamic acid which are described in this paper. The acid was prepared by hydrolysis of ethyl 2,4-dimethoxycinnamate made by the Claisen condensation and was the stable form.

We have found that addition of bromine to 2,4-dimethoxycinnamic acid is invariably accompanied by bromination in the ring, the position of the nuclear bromine atom being established by oxidation of the tribromo acid thus formed to 2,4-dimethoxy-5-bromobenzoic acid.' The behavior of the dimethoxycinnamic acid on bromination is, therefore, similar to that of **the** corresponding dimethoxybenzoylacrylic acid.[1] It has not been possible to prepare an unsaturated acid by elimination of hydrogen bromide from the tribromo acid by the usual methods. Invariably saturated alkoxy acids result which are probably formed by direct replacement of bromine by an

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[1] **Grace Potter Rice,** THIS JOURNAL, **48,3125** (1926).

alkoxyl group rather than by elimination of hydrogen bromide and addition of solvent. This is indicated by the fact that the tribromo acid is stable and does not lose hydrogen bromide below its melting point when heated alone nor when heated in high boiling solvents and that these same alkoxyl products are formed in alcoholic solution in the absence of an alkaline reagent. The ease of replacement of this bromine atom is comparable to that of the chlorine atom in unsaturated compounds containing the grouping $C_6H_5CHClCH{=}CH{-}{-}{-}{-}C_6H_5$. Straus[2] has found this chlorine atom to be increasingly labile with increasing unsaturation of the side chain and particularly with *p*-methoxy substituting groups. As it has been found during the course of previous work that such ease of replacement of bromine is not a characteristic of pmethoxy- nor of o-methoxycinnamic acid dibromide, with or without a bromine atom in the ring, this great lability of the bromine atom in the compounds under discussion must be ascribed to the presence of both para and ortho methoxyl groups, possibly also to the nuclear bromine atom. It is then, in all probability, the bromine atom adjacent to the ring that is replaced.

Since the usual esterification methods when used with the tribromo acid gave esters of alkoxy acids, the methyl ester of the tribromo acid was prepared by bromination of methyl 2,4-dimethoxycinnamate. Attempts to prepare the ethyl ester of the tribromo acid by bromination of ethyl 2,4-dimethoxycinnamate led to an interesting and unexpected result. Although the bromine and the solvent chloroform were the same as in the previous bromination reactions, the small amount of moisture evidently present hydrolyzed the product almost completely, the substance obtained in practically quantitative yield being 2,4-dimethoxy-5-bromobenzaldehyde. Even with dried reagents it has not as yet been possible to prepare a pure tribromo ethyl ester by this procedure. The crude product of the bromination gives the aldehyde when brought into contact with water. The tribromo acid and its methyl ester yield no trace of the aldehyde even on long boiling with water.

It seems reasonable to ascribe this difference in the behavior of the bromination product of the ethyl ester, on the one hand, and of the tribromo acid and its methyl ester on the other to a difference in space configuration. To test this assumption it would be necessary to prepare a tribromo ethyl ester, the diastereoisomer of the unstable one above postulated, which would be expected to have the characteristics of the tribromo acid and its methyl ester. It has been possible to prepare such an isomeric compound. Since the tribromo acid on treatment with diazomethane gave a tribromo methyl ester which, like the acid, was not hydrolyzed to the aldehyde, the tribromo acid was treated with diazoethane. As was expected, a tribromo ethyl ester resulted which behaved in all respects like the tribromo acid and

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[2] Straus and Diitzmann, *J. prakt. Chem.*, [2] **103**, 1 (1921).

its methyl ester. This ester has then undoubtedly the same space configuration as that of the tribromo acid. It may be considered to be derived from an ethyl-dimethoxycinnamate geometrically isomeric with the one from which the acid used in this study was prepared, which was made by the Claisen condensation, is pale yellow, melts at 68–69' and is hydrolyzed on bromination. When this ester was distilled under diminished pressure, a colorless solid melting at 61° was obtained. This is the isomeric ester. It does give on bromination the same tribromo ethyl ester that was obtained by action of diazoethane on the tribromo acid. The space relations of these esters are now under investigation.

Experimental Part

2,4-Dimethoxycinnamic acid was prepared from its ethyl ester obtained by Claisen condensation of 2,4-dimethoxybenzaldehyde and ethyl acetate according to the method of Perkin and Schiess,[3] which gives much better yields of the acid than the Perkin synthesis described by the same authors. 2,4-Dimethoxybenzaldehyde was prepared by the method used by Freudenberg[4] for veratric aldehyde. It was obtained in 85% yield and used without further purification. The resorcyl aldehyde needed in its preparation was obtained in good yield by the Gatterman method as modified by Johnson and Lane.[5]

The ethyl ester of 2,4-dimethoxycinnamic acid, melting at 68–69', obtained in a yield of 70% was saponified by boiling for an hour with an excess of 10% sodium hydroxide. The cooled solution on acidification deposited an 85–90% yield of the stable form of the corresponding acid. It was purified by crystallization from glacial acetic acid, which proved to give the purest product, although there was considerable loss of substance with this solvent.

Reaction of Bromine on 2,4-Dimethoxycinnamic Acid

Since it was not found possible to prepare a dibromo addition product of the acid, as bromination in the ring invariably accompanied the addition reaction, the following brominations were carried out with two molecular proportions of bromine.

2,4-Dimethoxy-5-bromocinnamic Acid Dibromide, $(CH_3O)_2BrC_6H_2CHBrCHBr$-COOH (I).—Fifteen grams of 2,4-dimethoxycinnamic acid was suspended in 250 cc. of chloroform, the mixture cooled and 8.2 cc. of bromine added slowly; the acid dissolved readily and, toward the end of the reaction, the bromo compound separated out. The mixture was shaken for a few minutes, the solid product then filtered and washed repeatedly with small amounts of cooled chloroform until it was practically colorless. By evaporation of the mother liquor in a current of dry air, further small amounts separated. The substance, obtained in practically quantitative yield, is a granular solid melting at 228–229° with vigorous decomposition. It is readily soluble in acetone and glacial acetic acid, very slightly soluble in chloroform, benzene and ether. As it was not found possible to purify it further by crystallization from any solvent, the carefully washed crude product was analyzed.

Anal. Subs., 0.1944: CO_2, 0.2110; H_2O, 0.0437. Calcd. for $C_{11}H_{11}O_4Br_3$: C. 29.54; H, 2.48. Found: C, 29.60; H, 2.52.

To determine the position of the nuclear bromine atom, the acid was oxidized with potassium permanganate. The product of the oxidation was proved to be 2,4-dimeth-

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[3] Perkin and Schiess, J. *Chem. Soc.*, 85,164 (1904).

[4] Freudenberg, *Ber.*, 53, 1416 (1920).

[5] Johnson and Lane, THIS JOURNAL, 43,348 (1921).

oxy-5-bromobenzoic acid by a mixed melting point with a sample of that acid obtained from another source.

Esterification of the tribromo acid was at first attempted in alcoholic solution but in all such reactions one bromine atom was replaced by an alkoxyl group. The methyl ester of 2,4-dimethoxy-5-bromocinnamic acid dibromide (II) was obtained by the reaction of the acid in ethereal solution with a slight excess of diazomethane. The ester crystallizes from the ether and can be purified from benzene or from ether, from which it separates in large firm crystals melting, with decomposition, at 142°.

Anal. Subs., 5.605 mg.: CO_2, 6.47 mg.; H_2O, 1.59 mg. Calcd. for $C_{12}H_{13}O_4Br_3$: C, 31.25; H, 2.84. Found: C, 31.48; H, 3.17.

Methyl Ester of **α-Bromo-β-methoxy-2,4-dimethoxy-5-bromohydrocinnamic** Acid, $(CH_3O)_2BrC_6H_2CH(OCH_3)CHBrCOOCH_3$ **(III)**.—This ester crystallized out from solution when the tribromo acid was allowed to stand overnight in methyl alcohol saturated with hydrogen chloride. It separates in compact, colorless crystals melting, without decomposition, at 149°.

Anal. Subs., 0.1695: CO_2, 0.2359; H_2O, 0.0628. Calcd. for $C_{13}H_{16}O_5Br_2$: C, 37.87; H, 3.91. Found: C, 37.95; H, 4.15.

This ester was also formed by recrystallization of the tribromo methyl ester (II) from boiling methyl alcohol and from the tribromo acid by allowing the acid to stand for several hours in contact with methyl alcohol. In the latter case the corresponding acid was also obtained.

α-Bromo-β-methoxy-2,4-dimethoxy-5-bromohydrocinnamic Acid **(IV)**.—The methyl alcoholic solution of the tribromo acid on standing overnight deposited a considerable quantity of the methyl ester (III) just described. The alcoholic solution was poured into aqueous sodium carbonate, this extracted with ether and the alkaline solution acidified. The heavy white precipitate was crystallized from benzene from which the acid separates in tiny shining hard crystals melting at 171° with effervescence and charring. From 1.0 g. of tribromo acid 0.6 g. of acid and 0.3 g. of methyl ester were obtained. This acid readily gives the ester (III) by action of diazomethane.

Anal. Subs., 5.069 mg.: CO_2, 6.77 mg.; H_2O, 1.77 mg. Calcd. for $C_{12}H_{14}O_5Br_2$: C, 36.19; H, 3.55. Found: C, 36.42; H, 3.91.

The ethyl ester (V) of the methoxy acid (IV) was obtained by the reaction of the acid in ethereal solution with diazoethane. The substance crystallizes from ethyl alcohol or from absolute ether in characteristic bunches of hexagonal plates. It melts at 109°.

Anal. Subs., 5.125 mg.: CO_2, 7.37 mg.; H_2O, 2.00 mg. Calcd. for $C_{14}H_{18}O_5Br_2$: C, 39.44; H, 4.23. Found: C, 39.22; H, 4.37.

The Ethyl Ester of **2,4-Dimethoxy-5-bromocinnamic** Acid Dibromide **(VI)**.—Five grams of freshly prepared tribromo acid was moistened with ether and a slight excess of freshly prepared diazoethane in ethereal solution added slowly. The acid dissolved readily and the ester began almost at once to separate from the solution as a pure white granular solid. It was filtered and washed with dry ether. The substance melts with vigorous effervescence at 158°. It is soluble in boiling benzene, very slightly soluble in ether and methyl and ethyl alcohols. With the latter solvents it reacts readily. It is very slightly soluble in boiling water and does not appear to react with it.

Anal. Subs., 4.766 mg.: CO_2, 5.77 mg.; H_2O, 1.26 mg. Calcd. for $C_{13}H_{15}O_4Br_3$: C, 32.85; H, 3.18. Found: C, 33.02; H, 2.96.

When this tribromo ethyl ester was boiled with methyl alcohol, the ethyl ester (V) of the methoxy acid (IV) was obtained. From ethyl alcohol the ethyl ester (VII) of the ethoxy acid (VIII) crystallized. The substance has, therefore, undoubtedly, the same configuration as the tribromo acid and its methyl ester.

The ethyl ester of α-bromo-β-ethoxy-2,4-dimethoxy-5-bromohydrocinnamic acid, $(CH_3O)_2BrC_6H_2CH(OC_2H_5)CHBrCOOC_2H_5$ (VII), was formed when the tribromo acid was treated with ethyl alcohol saturated with hydrogen chloride. It separates from ethyl alcohol in fine needles melting at 105–107°.

Anal. Subs., 0.1588: CO_2, 0.2384; H_2O, 0.0722. Calcd. for $C_{15}H_{20}O_5Br_2$: C, 40.91; H, 4.58. Found: C, 40.94; H, 4.96.

This ester was also obtained in small quantity when the tribromo acid was allowed to stand overnight with ethyl alcohol. As in the parallel reaction with methyl alcohol, the corresponding acid was also formed and was separated in the way there described.

α-Bromo-β-ethoxy-2,4-dimethoxy-5-bromohydrocinnamic Acid (VIII) crystallizes from benzene in small thick prisms melting at 161–162° with decomposition. By action of diazoethane on this acid, the ethyl ester (VII) is readily formed.

Anal. Subs., 6.140 mg.: CO_2, 8.49 mg.; H_2O, 2.16 mg. Calcd. for $C_{13}H_{16}O_5Br_2$: C, 37.87; H, 3.91. Found: C, 37.70; H, 3.94.

The methyl ester (IX) of the ethoxy acid (VIII) was obtained by the action of diazomethane on that acid and by crystallization of the methyl ester of the tribromo acid (II) from ethyl alcohol. It crystallizes readily from methyl alcohol or ether in rosets of firm needles melting at 138" with preliminary softening at 134°.

Anal. Subs., 6.167 mg.: CO_2, 8.98 mg.; H_2O, 2.29 mg. Calcd. for $C_{14}H_{18}O_5Br_2$: C, 39.44; H, 4.23. Found: C, 39.71; H, 4.15.

In marked contrast to the behavior of the dibromides of unsaturatated α-ketonic acids, which readily lose hydrogen bromide on heating or even spontaneously,[6] the tribromo acid above described did not lose hydrogen bromide to form an unsaturated acid under the usual conditions. It was recovered unchanged after heating at 100° and also after long heating in high-boiling solvents such as toluene, xylene and cymene. Action of potassium hydroxide in methyl alcoholic solution gave two products, a styrene derivative, as was to have been expected, and a small quantity of an acid, not however the corresponding unsaturated acid but the methoxy acid (IV). This same acid was formed by reaction of potassium acetate in methyl alcoholic solution.

1-Bromo-2-(2,4-dimethoxy-5-bromophenyl)-ethylene, $(CH_3O)_2BrC_6H_2CH{=}CHBr$ (X).—Five grams of the tribromo acid was stirred rapidly into 15 cc. of a saturated solution of potassium hydroxide in methyl alcohol. There was vigorous effervescence and a pasty solid separated. This was filtered, washed with a trace of alcohol and then repeatedly with water. The substance is readily soluble in the usual organic solvents. It separates from diluted methyl alcohol in clumps of fine white crystals melting at 67-68°. The yield was 80%.

Anal. Subs., 5.096 mg.: CO_2, 6.98 mg.; H_2O, 1.51 mg. Calcd. for $C_{10}H_{10}O_2Br_2$: C, 37.26; H, 3.10. Found: C, 37.35; H, 3.32.

The compound is very readily affected by the light. It rapidly takes on a rose pink color in diffused light and becomes black in a short time in bright sunlight. The aqueous washings from this substance on acidification yielded a small amount of the methoxy acid (IV). The styrene derivative (X) readily reacted further with bromine.

1,1-Dibromo-2-bromo-2-(2,4-dimethoxy-5-bromophenyl)-ethane, $(CH_3O)_2BrC_6H_2$-$CHBrCHBr_2$ (XI).—The substance separated from chloroform in quantitative yield as a slightly yellow powder, which after washing repeatedly with small amounts of cold methyl alcohol was colorless. It melts at 146° with slight effervescence.

Anal. Subs., 4.825 mg.: CO_2, 4.45 mg.; H_2O, 0.98 mg. Calcd. for $C_{10}H_{10}O_2Br_4$: C, 24.91; H, 2.09. Found: C, 25.15; H, 2.27.

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[6] Reimer, THIS JOURNAL, 48, 2454 (1926); Reimer and Howard, *ibid.*, 50, 2506 (1928).

This tetrabromo compound is perfectly stable when pure and does not change color on long standing. One of the four bromine atoms, presumably the one nearest the benzene ring, is very easily replaced by alkoxyl groups as in the case of the tribromo acid. On boiling the substance with methyl alcohol, in which it is only slightly soluble, a methoxy tribromo compound is formed.

1,1-Dibromo-2-methoxy-2-(2,4-dimethoxy-5-bromophenyl)-ethane, $(CH_3O)_2BrC_6H_2CH(OCH_3)CHBr_2$ **(XII)**.—The substance crystallizes from methyl alcohol or from ligroin in stiff prisms melting at 138–139°. The same substance was obtained by the action of potassium hydroxide in methyl alcoholic solution on the tetrabromo compound.

Anal. Subs., 4.965 mg.: CO_2, 5.55 mg.; H_2O, 1.27 mg. Calcd. for $C_{11}H_{13}O_3Br_3$: C, 30.48; H, 3.00. Found: C, 30.48; H, 2.86.

1,1-Dibromo-2-ethoxy-2-(2,4-dimethoxy-5-bromophenyl)-ethane, $(CH_3O)_2BrC_6H_2CH(OC_2H_5)CHBr_2$ **(XIII)**.—This substance is formed when the tetrabromo compound is boiled with ethyl alcohol. The product left after evaporation of the solvent was recrystallized from ligroin; melting point 117–120°.

Anal. Subs., 5.314 mg.: CO_2, 6.35 mg.; H_2O, 1.79 mg. Calcd. for $C_{12}H_{15}O_3Br_3$: C, 32.21; H, 3.36. Found: C, 32.59; H, 3.77.

Action of Bromine on the Esters of **2,4-Dimethoxycinnamic** Acid.—Methyl 2,4-dimethoxycinnamate was prepared by Claisen condensation by the same procedure as for the ethyl ester, and by the action of diazomethane on the acid. Either of these methods is simpler than that of Tiemann and Will.[7] It is most conveniently purified by distillation under diminished pressure. The pale yellow oil which distils at 216° (20 mm.) solidifies on cooling and, after one crystallization from methyl alcohol, is obtained in stiff colorless needles melting at 87°. Reaction of bromine on this ester gave, in quantitative yield, the tribromo ester (II) already described.

The ethyl ester of 2,4-dimethoxycinnamic acid behaved in an entirely different manner on treatment with bromine. The bromine was rapidly decolorized and on evaporation of the chloroform used as solvent, a yellow granular solid was left. This, after washing with benzene, was found to melt at 110–132°, showing it to be a mixture, and preliminary analysis gave 43.4% of carbon instead of 32.9% calculated for the expected tribromide. After purification, the product gave analytical results agreeing with those of an aldehyde, $(CH_3O)_2BrC_6H_2CHO$. That the product has this formula was proved by its ready oxidation with ammoniacal silver nitrate solution to 2,4-dimethoxy-5-bromobenzoic acid and by the preparation of its semicarbazone.

2,4-Dimethoxy-5-bromobenzaldehyde (XIV).—The substance is most readily obtained in pure condition by boiling the crude product of the bromination reaction with water. It separates from aqueous solution in a mass of very fine shining needles, from alcohol in sturdy needles or from benzene in branching clumps of fine thread-like crystals resembling a fungus growth. These after standing for some time crumble to small rhombic crystals. The substance melts without decomposition, 134–138°.

Anal. Subs., 5.468 mg.: CO_2, 8.90 mg.; H_2O, 1.74 mg. Calcd. for $C_9H_9O_3Br$: C, 44.08; H, 3.67. Found: C, 44.38; H, 3.56.

The semicarbazone is a fine white granular solid, very slightly soluble in methyl alcohol. It decomposes at about 275°.

Anal. Subs., 5.04 mg.: CO_2, 7.43 mg.; H_2O, 1.77 mg. Calcd. for $C_{10}H_{12}O_3N_3Br$: C, 39.74; H, 3.97. Found: C, 40.20; H, 3.93.

Since the preliminary analysis of the bromination product of ethyl 2,4-dimethoxycinnamate showed the product to be almost exclusively made up of the aldehyde, the

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[7] Tiemann and Will, *Ber.*, 15, 2079 (1882).

presence of the latter was attributed to water in the reagents which had presumably hydrolyzed the tribromo ethyl ester first formed in the reaction. The experiment was, therefore, repeated with carefully dried chloroform and bromine which had been distilled from phosphorus pentoxide. The product melted with decomposition over a long range, showing it to be probably a bromo addition compound but very impure. Repeated trials have not as yet given a pure substance. When this crude product was treated with water, a copious yield of the aldehyde was obtained.

When ethyl 2,4-dimethoxycinnamate (68–69°), prepared by the Claisen condensation, was distilled under diminished pressure, a yellow oil boiling at 219° (22 mm.) was obtained. This distillate solidified on cooling and, on crystallization from low boiling petroleum ether, separated in perfectly colorless needles melting at 61°. A mixture of this ester and the one previously used (68–69°) melted from 45–55°. Analysis proved it to be an isomeric form.

Anal. Subs., 0.1148: CO_2, 0.2777; H_2O, 0.0730. Calcd. for $C_{13}H_{16}O_4$: C, 66.10; H, 6.78. Found: C, 65.97; H, 7.05.

This isomeric ester on bromination with the usual laboratory reagents or with those that had been carefully dried gave, in quantitative yield, the ethyl ester of 2,4-dimethoxy-5-bromocinnamic acid dibromide (VI) previously described.

Summary

The bromination of 2,4-dimethoxycinnamic acid and its methyl and ethyl esters has been described. The acid differs from p-methoxycinnamic acid and from o-methoxycinnamic acid in the fact that addition of bromine is invariably accompanied by bromination in the ring and in the extraordinary ease of replacement of the β-bromine atom in the bromination products by alkoxyl groups. The two isomeric ethyl esters of the acid give different products on bromination.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE HALL LABORATORY OF CHEMISTRY, WESLEYAN UNIVERSITY]

BENZYLPINACOLONES AND THEIR REDUCTION PRODUCTS. I

BY G. ALBERT HILL AND WILLIAM F. BRUCE

RECEIVED JULY 29, 1929 PUBLISHED JANUARY 8, 1930

Sodamide syntheses,[1] in ether, with pinacolone and benzyl chloride yielded mono- and dibenzylpinacolones, $C_6H_5CH_2CH_2COC(CH_3)_3$, $(C_6H_5CH_2)_2CHCOC(CH_3)_3$. Benzylpinacolone has been described by one of us[2] but an improved method of preparation is reported here.

Dibenzylpinacolone in toluene reacted with sodamide and benzyl chloride producing tribenzylpinacolone, $(C_6H_5CH_2)_3CCOC(CH_3)_3$. Good yields resulted in this synthesis only when the original ketone, a readily purified crystalline solid, was distilled just prior to the runs. Possibly this is due to a higher proportion of an enolic modification in the freshly distilled material.

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[1] Haller and Bauer, *Ann. chim.*, [8] 29, 313 (1913).

[2] Hill, Spear and Lachowicz, THIS JOURNAL, 45, 1557 (1923).

Only the monobenzylpinacolone gave a crystalline oxime. Probably because of steric hindrance the more highly substituted ketones failed to react. All the ketones were reduced to the corresponding secondary alcohols by the action of sodium and absolute ethyl alcohol. Among the methods employed, which proved unattractive, were the use of sodium and amyl alcohol, sodium and moist ether, magnesium activated by mercuric chloride and absolute methyl alcohol, aluminum and solid potassium hydroxide in absolute ethyl alcohol and zinc and acetic acid.

Of the alcohols, only the tribenzyl derivative failed to give a crystalline phenylurethan.

The β-phenylethyl-*tert.*-butylcarbinol, $C_6H_5CH_2CH_2CHOHC(CH_3)_3$, is a liquid at room temperature. This is interesting because in the course of an earlier investigation of benzalpinacolone,[3] a compound was obtained which was thought to be this, then unknown, carbinol, but which melted at 142°. With the idea of reconciling these two reports, work on the substance melting at 142° has been resumed.

Attempts to reduce the ketones to the corresponding hydrocarbons by a wide variety of methods were unsuccessful save in the case of the monobenzyl compound. Heating with hydriodic acid and red phosphorus under pressure did, however, bring about reduction in this case. The Clemmensen method,[4] of which much was expected, gave only negative results.

Experiments with these ketones and alcohols, which it is hoped will yield the desired hydrocarbons, are being continued in this Laboratory.

It is a pleasure to acknowledge here the assistance in the preliminary work afforded by J. S. Lachowicz and E. W. Flosdorf, and gratefully to mention the material aid from the Atwater Fund.

Experimental Part

Pinacol Hydrate.—This was made according to Adams and Adams.[5]

Pinacolone.—The preparation was according to Hill and Flosdorf.[6]

The Ketones.—Mono-, di- and tribenzylpinacolones were prepared by methods essentially similar; therefore, the detailed procedure for the monobenzyl derivative only is given.

Monobenzylpinacolone.—A modification of the method of Hill and Lachowicz[3] was employed: 41 g. of finely ground friable sodamide was placed in a 2-liter, 3-necked flask provided with a reflux condenser, a mechanical stirrer with a mercury seal and a separatory funnel. A solution of 100 g. of pinacolone in 450 cc. of absolute ether was *slowly* introduced. The loss of ether and pinacolone swept out of the flask by the vigorous evolution of ammonia during the first half hour warranted the use of a trap bottle, im-

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[3] Ref. 2, p. 1561.

[4] Clemmensen, *Ber.*, 46, 1841 (1913).

[5] R. Adams and E. W. Adams, "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. V, 1925, p. 87.

[6] G. A. Hill and E. W. Flosdorf, *ibid.*, p. 91.

mersed in a freezing mixture, beyond the reflux condenser to collect the valuable pinacolone. The ether solution was boiled for from eight to ten hours, when evolution of ammonia had practically ceased; 132 g. of pure benzyl chloride was added very slowly, two or three drops a second, to avoid generation of too much ether vapor. The mixture was then warmed and stirred for twenty-four hours; 250 cc. of water was added and the ether layer removed, The latter was washed with water, dilute hydrochloric acid, and again with water, and dried with calcium chloride. After elimination of the ether, the residue was vacuum distilled: 106 g. of monobenzylpinacolone, a 56% yield, was obtained, accompanied by 60 g. of dibenzylpinacolone. These products account for 77.5% of the pinacolone used.

Monobenzylpinacolone is colorless when pure, and while insoluble in water dissolves readily in organic solvents; b. p. (10 mm.) 132"; (43 mm.) 155°; (760 mm.) 247°; d_{20}^{20} 0.95005; d_4^{20} 0.9483. The refractive index, n_D^{20}, is 1.4999. The dispersion factor found, $N_F - N_C$, is 0.01440. The molecular refraction, calculated by the Lorentz and Lorenz formula, is 58.8 while the values of Eisenlohr[7] give 58.6.

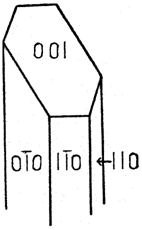
The oxime, prepared by Tanny's method,[8] melted at 95.5°, in agreement with the reported figure.

Dibenzylpinacolone.—The crude product was distilled, b. p. (9 mm.) 190–220°. The viscous yellow distillate solidified and after two crystallizations from ethyl alcohol melted at 49°. The yield of white crystalline material was 59%.

When pinacolone was treated with somewhat more than double the theoretical amount of sodamide and of benzyl chloride required for monosubstitution, a 66.6% yield of dibenzylpinacolone could be obtained without first isolating monobenzylpinacolone. An attempt to prepare an *oxime* was unsuccessful.

Anal. Subs., 0.1814, 0.1509: CO_2, 0.5691, 0.4743; H_2O, 0.1399, 0.1173. Calcd. for $C_{20}H_{24}O$: C, 85.66, H, 8.63. Found: C, 85.56, 85.69; H, 8.63, 8.70.

Crystal Structure of Dibenzylpinacolone.[9]—Triclinic system; prismatic habit. Positive unit prism 110; negative unit prism $1\bar{1}0$; side pinacoid 010. $110 > 1\bar{1}0 = 140° 33'$; $1\bar{1}0 > 010 = 97° 33'$; $110 > 0\bar{1}0 = 121° 52'$. Parameters: $a = 0.35735$; $b = 1.00000$; $c = 0.00000$. No good faces near 001 were obtained, but a conchoidal cleavage parallel to 001 was found.



Tribenzylpinacolone.—The apparatus used was similar to that previously described save that the stirrer passed through a close-fitting glass bearing tube, which extended into the solution, instead of through a mercury seal bearing. It was observed that when small amounts of mercury were prevented from passing into the reactants, the yields were better. Toluene was used as a solvent instead of ether. Pure tribenzylpinacolone was prepared by recrystallization from toluene, m. p. 161.5' (corr.). Yields as high as 73.4% were obtained.

Anal. Subs., 0.1983, 0.2372: CO_2, 0.6345, 0.7598; H_2O, 0.1442, 0.1721. Calcd. for $C_{27}H_{30}O$: C, 87.51; H, 8.17. Found: C, 87.26, 87.35; H, 8.14, 8.12.

The boiling point is (8 mm.) 268.9' (corr.). The calculated molecular weight is 370.2; found by Menzies' method, using benzene, 363.6, 365.2.[10]

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[7] Eisenlohr, *Z. physik. Chem.*, *75*, 585 (1911).

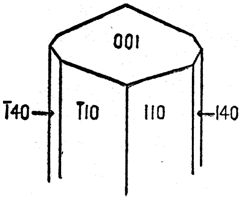
[8] Tanny, *Ber.*, 15, 2781 (1882).

[9] Studies of the crystal structures were made with the assistance of Professor W. G. Foye.

[10] Determination by B. C. French.

This ketone dissolves in toluene, quite readily when hot, but is only soluble to the extent of somewhat over 1 g. in 100 cc. of boiling alcohol. Boiling ether dissolves twice as much. It dissolves easily in hot carbon tetrachloride. An attempt to prepare an *oxime* was not successful.

Crystal Structure of Tribenzylpinacolone.—Orthorhombic system; columnar habit. Base 001; unit prism 110; brachyprism 140. 140 > $\bar{1}40$ = 131° 08′; 110 > $1\bar{1}0$ = 132° 45′; 110>140 = 138° 22′. Parameters: *a* = 0.043741; b = 1.00000; *c* = 0.00000. Fair basal cleavage, very good prism cleavage.



The Secondary Alcohols.—The most successful method employed for the reduction of the ketones to the corresponding secondary alcohols was ultimately used with all three, and hence the preparation of but one will be given in detail.

β-Phenylethyl-*tert*.-butylcarbinol.—Thirty-eight grams of monobenzylpinacolone dissolved in 280 cc. of absolute ethyl alcohol was treated, with stirring and refluxing, with 51 g. of sodium. This required about twenty minutes and stirring was continued for three hours; 200 cc. of water was added, and the resulting two-layer system separated. The aqueous part was made acid with hydrochloric acid and a small amount of oily material separated. This was added to the non-aqueous layer, which was washed with water, dilute hydrochloric acid and water, and after the addition of a little ether, about 50 cc., dried with sodium sulfate. By vacuum fractionation at 15.5 mm., the corrected boiling point was found to be 145.5′. and 28.5 g. of the carbinol, a yield of 73%, was procured.

Anal. Subs., 0.47680, 0.17990,[11] 0.26575; CO_2, 1.4144, 0.53380, 0.78810; H_2O, 0.44310, 0.16720, 0.24720. Calcd. for $C_{13}H_{20}O$: C, 81.18; H, 10.42. Found: C, 80.90, 80.93, 80.88; H, 10.40, 10.40, 10.40.

The carbinol is a colorless oily liquid insoluble in water and readily soluble in organic solvents; d_{20}^{20} 0.9593; d_4^{20} 0.9578; n_D^{20} 1.5097; $N_F - N_C$, 0.01456; M_D, calculated from the refractive index, 60.16; calculated from the Eisenlohr values, 60.158.

Preparation of the **Phenylurethan.**—Ten grams of the carbinol was mixed with 6.5 g. of phenylisocyanate and set aside, in a closed flask, for two days; 20 cc. of ethyl alcohol was then added and the flask warmed to bring about complete solution. On cooling the filtered material, microscopic white crystals separated, m. p. 88.1° (corr.).

Anal. (Kjeldahl). Subs., 0.5788, 0.5403: acid used, 20.56 cc. of 0.09232 *N*, 20.08 cc. of 0.08351 *N* H_2SO_4. Calcd. for $C_{20}H_{25}O_2N$: N, 4.50. Found: N, 4.58, 4.33.

(Dibenzylmethyl)-*tert*.-butylcarbinol.—This carbinol, b. p. (15 mm.) 206–208°, was obtained in a 32% yield.

And. Subs., 0.1998, 0.2068: CO_2, 0.6219, 0.6438; H_2O, 0.1636, 0.1694. Calcd. for $C_{20}H_{26}O$: C, 85.05; H, 9.28. Found: C, 84.90, 84.88; H, 9.17, 9.16.

This alcohol is colorless when pure, and is extremely viscous. Whiie it could be solidified, apparently, at low temperatures, it was not obtainable crystalline despite numerous and various attempts; d_{20}^{20} 1.005; n^{20}, using daylight, 1.5422, 1.5440; $N_F - N_C$, 0.01755. The phenylurethan was deposited as fine, white needles, m. p. 148".

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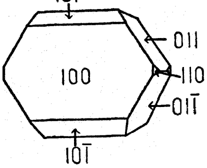
[11] Analysis by E. T. Dowling.

Anal. (Kjeldahl). Subs., 0.7512:[12] acid used, 18.34 cc. of 0.10372 N H_2SO_4. Calcd. for $C_{27}H_{31}O_2N$: N, 3.49. Found: N, 3.54.

(Tribenzylmethyl)-*tert.*-butylcarbinol.—Some of this carbinol was prepared by the action of sodium and amyl alcohol on the ketone, but the method was no better than the foregoing, which, in the presence of a little toluene, gave a yield of 45%, m. p. 156.5° (corr.). An attempt to form a phenylurethan was unsuccessful.

Anal. Subs., 0.2418, 0.2868: CO_2, 0.7723, 0.9137; H_2O, 0.1869, 0.2203. Calcd. for $C_{27}H_{32}O$: C, 87.03; H, 8.67. Found: C, 86.94, 86.88; H, 8.65, 8.60.

Crystal Structure of (Tribenzylmethyl)-*tert.*-butylcarbinol.—Orthorhombic system; tabular habit, Front pinacoid 100; brachydome 011; macrodome 101; indistinct unit prism 110. 011 > $01\bar{1}$ = 93° 15'; 011 > $0\bar{1}1$ = 86° 45'; 100 > 101 = 135° 33'; 101 > $\bar{1}01$ = 88° 46'. Parameters: a = 0.94482; *b* = 1.00000; c = 1.0218.



The Hydrocarbons.—Despite numerous and various attempts to reduce the ketones and carbinols to hydrocarbons, only that derived from the monobenzyl compound has been obtained.

2,2-Dimethyl-5-phenyl-pentane.—Nine and one-half grams of monobenzylpinacolone, 1.7 g. of red phosphorus and 25.6 g. of 57% hydriodic acid were heated to 180–190° in a sealed tube for twelve hours. The contents of the cooled tube was placed in 150 cc. of 1:15 sulfuric acid and mossy zinc was added. After one and one-half hours the product was removed by ether, the ether solution was washed with water, dilute sodium hydroxide, and water, and dried with calcium chloride. Upon repeated fractionation, after removal of the ether (4 g.) a 46% yield of hydrocarbon resulted; b. p. (9 mm.) 115".

Anal. Subs., 0.1701, 0.2218, 0.1592, 0.2030: CO_2, 0.5555, 0.7243, 0.5192, 0.6571; H_2O, 0.1584, 0.2063, 0.1479, 0.1882. Calcd. for $C_{13}H_{20}$: C, 88.55, H, 11.44. Found: C, 89.06, 89.06, 88.94, 88.28; H, 10.41, 10.43, 10.40, 10.40.

The pure substance was colorless and an acetone solution of potassium permanganate was only very slowly reduced when in contact with it. Molecular weight, calcd. for $C_{13}H_{20}$: 176.16; found, by Menzies' method, 189, 178; d^{20}_{20} 0.9460; d^{20}_{4} 0.9443; n^{20}, using daylight, 1.5281, 1.5267; $N_F - N_C$, 0.01615; M_D, from refractive index, 57.39; from Eisenlohr's values, 58.63.

Summary

1. Mono-, di- and tribenzylpinacolones, a series of highly substituted acetones, and their corresponding secondary alcohols have been prepared.
2. One hydrocarbon, 2,2-dimethyl-5-phenyl-pentane, related to the simplest of the ketones, has been produced.
3. Experiments leading to the other hydrocarbons are in progress.

MIDDLETOWN, CONNECTICUT

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[12] Analysis by F. H. Adams.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF SWARTHMORE COLLEGE]

THE MECHANISM AND APPLICATION OF THE FRIES REACTION[1]

BY EDWARD H. COX

RECEIVED JULY 29, 1929 PUBLISHED JANUARY 8, 1930

The rearrangement of the phenolic esters to hydroxy aromatic ketones by means of anhydrous aluminum chloride (the Fries reaction) has been observed by many workers.[2] Although aluminum chloride is the most effective reagent used in carrying out these rearrangements, anhydrous ferric chloride and, especially, zinc chloride are only slightly less efficient.[3]

Fries, Witt[4] and recently Auwers[5] have considered the reaction to be intramolecular. Skraup and Poller[6] prepared o-acetyl-m-cresol by the action of anhydrous zinc chloride on m-tolyl acetate and contended that the ester was first decomposed by the zinc chloride into acetyl chloride and m-cresol and that the acid chloride then reacted with the cresol to form the ketone. They repeated this reaction but added m-chlorobenzoyl chloride and observed that this acid chloride reacted with the cresol at the expense of the more volatile acetyl chloride. Only m-chlorobenzoyl-m-cresol (2-hydroxy-4-methyl-3'-chlorobenzophenone) was produced; no *o*-acetyl-*m*-cresol was isolated. Auwers and Mauss[7] have contrasted the Fries reaction with that of Friedel–Crafts when applied to phenols, and have drawn a distinction according to whether the acid residue is introduced from without the molecule or is originally present, as is the case in the Fries rearrangements. Since, according to these workers, the Friedel–Crafts reaction when applied to most phenols, in the preparation of aromatic hydroxy ketones, generally gives the *p*-acylphenols,[8] and with a few phenols of certain structure, the meta derivatives, and since on the other hand in the Fries reaction only ortho or para and never m-acylphenols are produced, then the Fries displacement according to them is considered to take place within the molecule (intramolecular).

Rosenmund and Schnurr[9] studied the conditions of the Fries transformation in order to improve upon the method. They have discussed

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[1] A preliminary report of this work was made at the Richmond, Virginia, meeting of the American Chemical Society, April, 1927, under the title "Mechanism of the Fries Reaction."

[2] Fries and co-workers, *Ber.*, 41, 4276 (1908); 43, 214 (1910); 54, 717 (1921); 56, 1305 (1923); Auwers, Ann., 421, 36 (1920); 447, 162 (1926).

[3] Eijkman, *Chem. Weekblad*, 1, 455 (1904); Heller, *Ber.*, 42, 2738 (1909); 45, 418, 2389 (1912).

[4] Witt and Braun, *ibid.*, 47, 3219 (1914).

[5] Auwers and Mauss, *Ann.*, 464, 293 (1928).

[6] Skraup and Poller, *Ber.*, 57, 2033 (1924).

[7] Auwers and Mauss, *ibid.*, 61, 1495 (1928).

[8] Auwers and Mauss, *Ann.*, 464, 295 (1928).

[9] Rosenmund and Schnurr, *ibid.*, 460, 56 (1928).

their experimental results and have disagreed with Auwers' statement that the reaction is intramolecular. They have found that when a mixture of o-chloro-p-tolyl acetate (2-chloro-4-methylphenyl acetate) and p-tolyl benzoate is acted upon by aluminum chloride, not only 2-acetyl-6-chloro-*p*-cresol (2-hydroxy-3-chloro-5-methylacetophenone) and *o*-benzoyl-*p*-cresol (2-hydroxy-5-methylbenzophenone) are formed, but also 2-benzoyl-6-chloro-p-cresol (2-hydroxy-3-chloro-5-methylbenzophenone) and *o*-acetyl-p-cresol (2-hydroxy-5-methylacetophenone). They state that if this reaction were strictly intramolecular, the latter two compounds should not have been formed. These authors have also taken exception to Skraup's explanation of the reaction, for they were unable to distil out any free acid chloride, even when working at reduced pressure and in a stream of hydrogen. They have interpreted the mechanism of the Fries change as one involving two molecules of the ester and have likened the reaction to that of Friedel–Crafts where acetic anhydride is the acetylating reagent. The possibility of free radical exchange is also indicated.

The experimental results given in this paper support the contention of Skraup and Poller, *viz.*, that, when phenolic esters are acted upon by anhydrous aluminum or zinc chlorides, the free acid chlorides are produced which then act upon the phenolic group, giving ketones. If the change were intramolecular there should be the possibility of the formation and isolation of some intermediate product. The failure to identify any such product and the results of Rosenmund and Schnurr's work are contrary to the interpretation that the transformation takes place within the ester molecule. That there is no exchange of free radicals is supported by the fact that a catalyst is necessary for the transformation.[10] That the Fries change is comparable to the Friedel–Crafts reaction when acetic anhydride is used is not untenable, since the action of aluminum chloride on acetic anhydride produces acetyl chloride.

In the first part of the experimental work recorded here the Fries reaction is carried out in the relatively inert solvent, diphenyl ether. When anhydrous aluminum or zinc chloride acts upon phenolic esters in the presence of this solvent, the acyl phenols and acyl diphenyl ether are both formed. It is difficult to interpret the formation of the acyl derivative of diphenyl ether other than that it is produced by the medium of the free acid chloride. Some free phenol is invariably recovered from the reaction mixture.

It has also been observed during the course of some experimental work that, if absolute alcohol was added during the reaction of anhydrous aluminum chloride on tolyl acetates, ethyl acetate was distilled from the re-

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[10] Skraup [Skraup and co-workers, *Ber.*, 60, 942, 1070 (1927)] has carried out some pyrolytic reactions on special phenyl esters at high temperatures (350–420°) but the yields of the ketones were very low. When the reactions were carried out in the presence of anhydrous zinc chloride and halogen acids much lower temperatures were required and higher yields of ketones were obtained.

action mixture. Again, in an attempt to rearrange these acetates under pressure, using absolute alcohol containing hydrogen chloride as a solvent, ethyl acetate was found to be one of the reaction products. Finally, it was observed that some acetyl chloride was distilled out when aluminum chloride acted on 2,4,6-trichlorophenyl acetate. These observations support the conclusion that the free acid chloride is an intermediate in the Fries reaction.

That the reaction gives better yields of aromatic hydroxy ketones than are obtained by the Friedel–Crafts method may be explained by the fact that a less amount of aluminum chloride is necessary to effect the transformation and that the progressive splitting and resubstituting of the acyl group give rise to more ideal concentration of the reactants.

In the second part of the experimental work the Fries reaction is applied in the preparation of some acyl derivatives of salicylic acid. The esters of methyl salicylate are prepared by the action of acid chlorides on methyl salicylate, and are transformed by anhydrous aluminum chloride to the acyl salicylates. The acyl esters are then saponified and subsequently reduced to the alkyl salicylic acids by the Clemmensen method. In view of the general interest manifested in the relation of the alkyl phenolic substances to their antiseptic properties and because most of the substances are not given in the literature, it is considered of value to record them.

Experimental. Part I

A general statement of the experimental procedure is as follows: to 40 g. of anhydrous aluminum chloride was added 200 cc. of carbon disulfide. To these was added slowly with heating and stirring a mixture of 50 g. of the phenolic ester and 60 g. of diphenyl ether. After the addition, the reaction mixture was heated for a short time and the carbon disulfide was then distilled off. The temperature was raised from 100–175° for fifteen to forty-five minutes. The reaction melt was decomposed in water and the resulting oily layer separated, treated with a 15% solution of potassium hydroxide and extracted with ether. The aqueous portion was acidified with dilute hydrochloric acid solution and also extracted with ether. Both ether extracts were dried, evaporated and distilled in a vacuum.

Action of Aluminum Chloride on *m*-Tolyl Butyrate in Diphenyl Ether.—The reaction mixture was heated to 100–110° for fifteen to twenty minutes. The alkali-insoluble portion was distilled in a vacuum. Fraction one, boiling from 140–150° at 20 mm., was unchanged diphenyl ether (42 g.); fraction two, boiling from 200–208° at 12 mm., was *p*-butyryl diphenyl ether (24 g.). The second fraction solidified and was crystallized from petroleum ether (m. p. 50").

Anal. Subs., 0.1336: CO_2, 0.3931; H_2O, 0.0804. Calcd. for $C_{16}H_{16}O_2$: C, 80.00; H, 6.66. Found: C, 80.24; H, 6.73.

Fraction one of the alkali-soluble portion, distilling from 100–135° at 25–30 mm., was m-cresol (18 g.) and was identified as the benzoate (m. p. 54–55'). Fraction two, distilling from 175–200° at 15 mm., was *p*-butyryl-*m*-cresol, $C_6H_3(OH)(CH_3)(COC_3H_7)$ (1 3 4) The distillate soon solidified and was crystallized from a mixture of benzene and petroleum ether (m. p. 88°).

Anal. Subs., 0.1632: CO_2, 0.4422; H_2O, 0.1143. Calcd. for $C_{11}H_{14}O_2$: C, 74.15; H, 7.86. Found: C, 73.89; H, 7.84.

Action of Aluminum Chloride on *o*-Tolyl Acetate in Diphenyl Ether.—The reaction mixture was heated for thirty minutes at 175°. The alkali-insoluble portion yielded 54 g. of unchanged diphenyl ether and 14 g. of *p*-acetyl diphenyl ether, distilling from 180–190° at 7 mm. It was crystallized from petroleum ether and melted at 53°.[11]

Anal. Subs., 0.1254: CO_2, 0.3629; H_2O, 0.0764. Calcd. for $C_{14}H_{12}O_2$: C, 79.24; H, 5.66. Found: C, 78.91; H, 6.01.

The alkali-soluble portion yielded 18 g. of o-cresol, identified as the *p*-nitrobenzoate (m. p. 90–92°), and 27 g. of *p*-acetyl-*o*-cresol, $C_6H_3(OH)(CH_3)(COCH_3)(1,2,4)$, distilling from 170–175° at 5 mm. It was crystallized from a mixture of benzene and petroleum ether and melted at 110°.[12]

Anal. Subs., 0.2043: CO_2, 0.5380; H_2O, 0.1253. Calcd. for $C_9H_{10}O_2$: C, 72.00; H, 6.66. Found: C, 71.81; H, 6.86.

Action of Aluminum Chloride on *p*-Tolyl Acetate in Diphenyl Ether.—The reaction mixture was heated for fifteen minutes at 160°. The alkali-insoluble portion yielded 46 g. of unchanged diphenyl ether and 11 g. of p-acetyl diphenyl ether. The latter compound when mixed with the acetyl diphenyl ether from the above experiments showed a melting point of 52–53°.

The alkali-soluble portion yielded a small amount of *p*-cresol and 15 g. of *o*-acetyl-*p*-cresol, $C_6H_3(OH)(CH_3)(COCH_3)(1,4,2)$, distilling from 120–130° at 7 mm. After crystallization from petroleum ether it melted at 48–49°.[13] An alcoholic solution of the ketone gave a purple color with a few drops of ferric chloride solution.

Anal. Subs., 0.1674: CO_2, 0.4402; H_2O, 0.1025. Calcd. for $C_9H_{10}O_2$: C, 72.00; H, 6.66. Found: C, 71.71; H, 6.85.

Action of Aluminum Chloride on o-Tolyl Benzoate in Diphenyl Ether.—The reaction mixture was heated to 170° for thirty minutes. The ether extract from the alkali-insoluble portion was evaporated. The residue was treated with cold petroleum ether, which separated the diphenyl ether from the *p*-benzoyl diphenyl ether (34 g. of the former and 14 g. of the latter were recovered). The ketone was crystallized from ligroin and melted at 71–73°.[11]

Anal. Subs., 0.1192: CO_2, 0.3641; H_2O, 0.0575. Calcd. for $C_{19}H_{14}O_2$: C, 83.21; H, 5.11. Found: C, 83.01; H, 5.03.

The ether extract from the alkali-soluble portion was evaporated and yielded 34 g. of *p*-benzoyl-*o*-cresol, $C_6H_3(OH)(CH_3)(COC_6H_5)(1,2,4)$, and a small amount of o-cresol. The ketone was crystallized from benzene and melted at 173°.[14]

Anal. Subs., 0.1708: CO_2, 0.4949; H_2O, 0.0850. Calcd. for $C_{14}H_{12}O_2$: C, 79.24; H, 5.66. Found: C, 79.02; H, 5.57.

Experimental. Part II

All the fatty acid esters of methyl salicylate were made by treating the oil of wintergreen with the respective fatty acid chlorides. The reactions were carried out at about the boiling temperature of the acid chloride and over a period of about two hours, or until all the hydrogen chloride was

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[11] Kipper, ***Ber.***, 38, 2491 (1905).

[12] Nencki and Stroeber, *ibid.*, 30, 1770 (1897).

[13] Auwers, *Ann.*, **364**, 166 (1908).

[14] Heller, ***Ber.***, **46**, 1502 (1913).

dispelled. The esters were purified by treatment with dilute sodium bicarbonate solution and distillation in a vacuum. They were considered pure when they showed no blue color with a few drops of ferric chloride solution. The yields averaged about 90%.

Since there were no essential variations in the experimental procedure used for the preparation of the members of these series, but one member of each series will be given in detail, *viz.*, hexylyl and hexylsalicylic acids. The melting points, boiling points and analyses of the different members will be shown in tabular review.

All of the ketones when dissolved in dilute alcohol gave a deep red coloration with a few drops of a solution of ferric chloride, while the reduced products showed a blue color. Reduction of the ketones was considered complete when the ferric chloride test showed a distinct blue color.

Methyl **Hexylyl-salicylate,** $C_6H_3(OH)(COOCH_3)(COC_5H_{11})(1,2,4)$.—To a suspension of 125 g. of anhydrous aluminum chloride in 200 cc. of boiling carbon disulfide was slowly added with stirring 150 g. of caproate of methylsalicylate (b. p. 204–210° at 20 mm.). After two hours of heating, the carbon disulfide was distilled off and the reaction mixture heated for a few minutes. The mass soon hardened and became impossible to stir (from 90–110°). The melt was decomposed in warm water and the resulting oily layer was washed with hot water, separated and distilled in a vacuum. After distilling off the water, two fractions were separated, one, boiling from 120–170° at 20 mm. (mostly unchanged material) and two, boiling from 210–230° at 20 mm. A small amount of residue remained in the flask. The distillate from fraction two soon solidified. A further recovery from fraction one gave a total yield of 123 g., or 82%. It was crystallized twice from petroleum ether and melted at 50–51°. It formed insoluble sodium and potassium salts. The ketone distilled from 202–205" at 20 mm.

TABLE I

METHYL ACYL-SALICYLATES

			M. p., °C.
1	Methyl propionyl-salicylate	$C_6H_3(OH)(COOCH_3)(COC_2H_5)$	64–65
2	Methyl butyryl-salicylate	$C_6H_3(OH)(COOCH_3)(COC_3H_7)$	73
3	Methyl iso-hexylyl-salicylate	$C_6H_3(OH)(COOCH_3)(COC_5H_{11})$	Liquid, b. p. 195–198, 15 mm.
4	Methyl hexylyl-salicylate	$C_6H_3(OH)(COOCH_3)(COC_5H_{11})$	50–51

ANALYSES

	Subs., g.	CO_2, g.	H_2O, g.	Calcd., % C	H	Found, % C	H
1	0.1437	0.3314	0.0797	63.46	5.77	62.89	6.26
2	.2140	.5096	.1244	64.86	6.30	64.94	6.50
3	.1500	.3692	.1013	67.20	7.20	67.12	7.55
4	.1924	.4719	.1287	67.20	7.20	66.89	7.48

Hexylyl Salicylic **Acid,** $C_6H_3(OH)(COOH)(COC_5H_{11})(1,2,4)$.—Methyl hexylyl-salicylate was hydrolyzed in a boiling 20% solution of potassium hydroxide. The free acid was precipitated from the potassium salt by hydrochloric acid solution, filtered, dried and crystallized from a mixture of benzene and petroleum ether. After two crystallizations it melted at 117°.

TABLE 11

ACYL SALICYLIC ACIDS

			M. p., °C.
1	Propionyl salicylic acid	$C_6H_3(OH)(COOH)(COC_2H_5)$	177–179
2	Butyryl salicylic acid	$C_6H_3(OH)(COOH)(COC_3H_7)$	152–153
3	*Iso*-hexylyl salicylic acid	$C_6H_3(OH)(COOH)(COC_5H_{11})$	132–133.5
4	Hexylyl salicylic acid	$C_6H_3(OH)(COOH)(COC_5H_{11})$	117

ANALYSES

	Subs., g.	CO_2, g.	H_2O, g.	Calcd., %		Found, %	
				C	H	C	H
1	0.1866	0.4217	0.0876	61.85	5.15	61.63	5.31
2	.1688	.3931	.0882	63.46	5.77	63.51	5.84
3	.1582	.3819	.0984	66.10	6.78	65.83	6.96
4	.1499	.3618	.0947	66.10	6.78	65.82	7.06

Hexyl Salicylic Acid,[15] $C_6H_3(OH)(COOH)(C_6H_{13})$ (1,2,4).—Hexylyl salicylic acid was reduced smoothly by zinc amalgam in one to one hydrochloric acid solution. One hundred grams of the ketone was reduced in five hours by 500 g. of zinc amalgam in 800 cc. of dilute acid solution. Reduction was considered complete when a few drops of the oily reaction product dissolved in alcohol showed a dark blue color upon the addition of a few drops of ferric chloride solution. The oily reduced product solidified on cooling. It was washed with hot water, dried and crystallized from ligroin. The acid melted at 83–84'. The crude product weighed 83.5 g., a yield of 88%.

TABLE III

ALKYL SALICYLIC ACIDS

			M. p.. °C.
1	Propyl salicylic acid	$C_6H_3(OH)(COOH)(C_3H_7)$	99–100
2	Butyl salicylic acid	$C_6H_3(OH)(COOH)(C_4H_9)$	84–86
3	*Iso*-hexyl salicylic acid	$C_6H_3(OH)(COOH)(C_6H_{13})$	104–105
4	Hexyl salicylic acid	$C_6H_3(OH)(COOH)(C_6H_{13})$	83–84

ANALYSES

	Subs., g.	CO_2, g.	H_2O, g.	Calcd., %		Found, %	
				C	H	C	H
1	0.1441	0.3511	0.0884	66.66	6.66	66.46	6.86
2	.1341	.3326	.0896	68.04	7.21	67.64	7.47
3	.1486	.3810	.1065	70.27	8.10	69.92	8.01
4	.1400	.3608	.1032	70.27	8.10	70.28	8.24

I wish to express my thanks to Dr. George W. Raiziss of the Dermatological Research Laboratories, Philadelphia, for his part in making the biological tests.

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[15] Swiss Patent 127,649 (1927).

Summary

The Fries reaction is discussed and an explanation of the mechanism is given based upon some experimental evidence. The reaction is shown not to be intramolecular. It has been applied to the production of some acyl salicylic esters and acids, many of which are new substances.

The alkyl salicylic acids are produced from the acyl salicylic acids by the Clemmensen reduction method. Although these acids show a higher toxicity than the parent substance, salicylic acid, they also possess by virtue of the alkyl group higher phenol coefficients.

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[CONTRIBUTION NO. 64 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

THE OXIDATION OF META-XYLORCINOL[1]

BY TENNEY L. DAVIS AND JOSEPH FREDERIC WALKER

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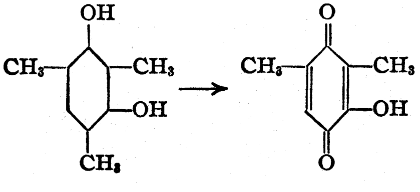
When tribromoresorcinol is oxidized with aqueous chromic acid[2] it does not yield a *m*-quinone, but loses a bromine atom from the position para to one of the hydroxyl groups and yields oxidized and brominated substances which are derivatives of diphenoquinone. We have wished to determine whether a methyl group in the para position would be similarly lost, and have accordingly studied the oxidation of m-xylorcinol in which both positions para to hydroxyl are occupied by methyl groups. A similar substance has been studied by Knecht,[3] who found that the action of hot ferric chloride solution on mesorcinol removed a methyl group from the para position and produced a derivative of benzoquinone, thus



It is apparent from Knecht's result that one of the methyl groups is more easily removed by oxidation than is the hydrogen of one of the hydroxyl groups. When tribromoresorcinol is oxidized, the bromine in one of the para positions is similarly removed and one of the hydroxyl groups remains unaffected. m-Xylorcinol differs from mesorcinol in having a hydrogen instead of a methyl in the position between the two hydroxyl groups, and it is to be expected that this particular hydrogen atom would be oxi-

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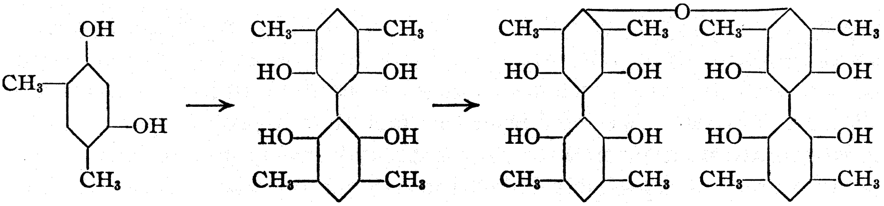
[1] A summary of the Doctor's Dissertation of Joseph Frederic Walker, Massachusetts Institute of Technology, June, 1929.

[2] Davis and Hill, THIS JOURNAL, 51, 493 (1929).

[3] Knecht, *Ann.*, 215, 96 (1882).

dized fairly easily, surely more easily than a methyl group. We find, in fact, that the methyl and hydroxyl groups of m-xylorcinol are not affected by dilute aqueous ferric chloride solution at laboratory temperature. One hydrogen atom, presumably the hydrogen which is present in m-xylorcinol but is lacking in mesorcinol, is, however, removed from the nucleus, and two nuclei combine to form di-m-xylorcinol. This product, soluble in water, is oxidized by the further action of ferric chloride to form an insoluble substance which appears to be di-(di-m-xylorcinol) ether.



m-Xylorcinol has been studied but little, probably because of the difficulty of its preparation. In the course of our work we have prepared from more than 2 kilos of m-xylene, a total of 15 g. of m-xylorcinol. We have checked the work of previous investigators and have substantiated the formula by determinations of molecular weight in benzene and in camphor. The substance is a vigorous reducing agent. If a 1% aqueous solution of m-xylorcinol is mixed with its own volume of 0.1 *N* silver nitrate, the liquid after about three minutes becomes colored from colloidal silver, and on longer standing deposits a silver mirror on the walls of the tube. Cresorcinol, in which there is a methyl group para to only one of the hydroxyl groups, under similar conditions shows no effect until about fifteen minutes have elapsed, and resorcinol itself shows none after twenty-four hours.

When a drop of ferric chloride solution is added to a dilute aqueous solution of m-xylorcinol a deep blue coloration is produced which disappears in a few minutes and leaves a pale green turbidity. On standing a voluminous greenish precipitate settles out. This behavior—similar to that observed by Dianin,[4] who reported that ferric chloride gave with solutions of α- and β-naphthol a color which vanished almost instantly with the appearance of a white precipitate—suggests that the hydrogen atom which is oxidized is that which occupies the position next to an hydroxyl group, or, in our case, between the hydroxyl groups, for Walder[5] and Fosse[6] later showed that the products from Dianin's experiments are dinaphthols in which the residues are linked through the position ortho to the hydroxyl group.

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[4] Dianin, J. *Russ. Phys.-Chem. Soc.*, 6, 187 (1873).

[5] Walder, *Ber.*, 15, 2166 (1882).

[6] Fosse, *Bull. soc. chim.*, [3] 21, 650 (1899).

The first product of the oxidation is a crystalline substance, soluble in water, and was obtained by extracting the filtered liquid with ether, or in better yields by shaking an ether solution of *m*-xylorcinol with an aqueous solution of ferric chloride. It is dinuclear and forms a tetra-acetate. It dissolves readily in sodium hydroxide solution, but not in sodium bicarbonate, and it gives Liebermann's nitroso reaction for *m*-diphenols. It precipitates metallic silver from ammoniacal silver nitrate, and with ferric chloride it yields the insoluble material which we believe to be di-(di-m-xylorcinol) ether. When distilled with zinc dust it yields a substance which is probably dixylyl. When di-m-xylorcinol is heated for three minutes at 160° with phthalic anhydride and a drop of concd. sulfuric acid, it gives a melt which dissolves in alkali to form a practically colorless solution. We infer from this fact that it probably contains no hydrogen atom either ortho or para to an hydroxyl group, and hence that the two nuclei are probably linked through the position between the two hydroxyl groups.

m-Xylorcinol contains one hydrogen atom which is readily replaceable by bromine, but this same atom appears to be lacking from di-m-xylorcinol and is evidently the atom through the removal of which the two nuclei are joined. m-Xylorcinol brominates easily in chloroform solution to form the monobromo-m-xylorcinol which was described by Luther.[7] When this substance is heated gently with a trace of sulfuric acid, it evolves hydrogen bromide vigorously—a fact which suggests that the bromine atom is in a position ortho to an hydroxyl group. Di-m-xylorcinol reacts with bromine in boiling chloroform solution to yield colorless needles of a product which analyses and molecular weight determinations show to be not a simple bromine substitution product. The product dissolves slowly in caustic alkali and reprecipitates on acidification; the solution after acidification contains no ionized bromine. It does not give Liebermann's reaction for m-diphenols. It reduces ammoniacal silver nitrate slowly in the cold, and rapidly when the liquid is heated. Its analysis, etc., correspond, unexpectedly and unexplainably, to di-m-xylorcinol in which two of the hydroxyl groups have been replaced by bromine atoms. In confirmation of the belief that the hydroxyl groups are involved in the reaction with bromine, we find that the tetra-acetate of di-m-xylorcinol does not react when boiled with two molecules of bromine in chloroform solution.

When a drop of ferric bromide solution is added to a dilute aqueous solution of monobromo-m-xylorcinol, a momentary violet coloration is produced which is followed by a white turbidity. After a few minutes a white precipitate settles out. The appearance of the reaction suggests that the changes are analogous to those which occur with m-xylorcinol,

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[7] *Luther, Arch. Pharm., 244,561 (1906).*

but such is not the case. The crystalline product does not give Liebermann's reaction and does not yield an acetate by the usual procedure. It dissolves readily in dilute sodium hydroxide to form a solution which contains ionized bromine. It liberates a small amount of iodine from alcoholic potassium iodide to which a drop of hydrochloric acid has been added, and it reduces ammoniacal silver nitrate immediately in the cold. Analysis and molecular weight determinations show that it contains two bromine atoms, but it does not have the composition of dibromo-di-*m*-xylorcinol, and is not identical with the substance obtained by the action of bromine on di-*m*-xylorcinol.

Under the conditions in which m-xylorcinol is oxidized by ferric chloride to di-*m*-xylorcinol in maximum yield, cresorcinol yields no oxidation product and is recovered unchanged.

Experiments

Preparation of *m*-Xylorcinol.—*m*-Xylene was nitrated according to the method of Maltese and Errera[8] and the 4,6-dinitroxylene-1,3 was separated by fractional crystallization from alcohol as light yellow needles with a faint greenish glow, m. p. 93°. Maltese and Errera reported a yield of about one-third, but we were not able to obtain more than a 12% yield of the pure product. The other steps in the synthesis were slight modifications of the procedure originally employed by Pfaff.[9] Reduction in the usual way with hydrogen sulfide and alcoholic ammonia gave 4-nitro-6-aminoxylene-1,3, orange needles from alcohol, m. p. 122–123° (90%), and this by the diazo reaction gave 4-nitro-6-hydroxyxylene-1,3 as yellow needles from ligroin, m. p. 95° (65%). The nitrophenol was reduced with tin and hydrochloric acid and the 4-amino-6-hydroxyxylene-1,3 was isolated in the form of its hydrochloride (70%). In the diazo reaction for the replacement of the second amino group by hydroxyl it was found that the use of copper sulfate as a catalyst increased the yield from about 47 to 60%. The m-xylorcinol, obtained by extracting the boiled and filtered diazo solution with ether, decolorizing the product in water solution with decolorizing carbon and finally purifying by sublimation at 120" and 3 mm., consisted of colorless needles, m. p. 124.5–125.2". The yields indicated above are the yields in our best experiments and correspond to an over-all yield of 2.95% of the theoretical amount of m-xylorcinol from m-xylene. When the product was heated at 160° for three minutes with phthalic anhydride and a drop of sulfuric acid, it gave a melt which dissolved in alkali to give a dark brown solution possessing a deep green fluorescence. A similar experiment without phthalic anhydride gave, contrary to the report of Pfaff, a faint mauve-colored solution which showed only a very slight fluorescence.

Molecular weight. Subs., 0.0866, 0.1922 g.; benzene, 17.27, 17.27 g.; *AT*, 0.099°, 0.215". Calcd. for $C_8H_{10}O_2$: 138. Found: 135, 138. Subs., 0.0141 g.; camphor, 0.1158 g.; AT, 35.7°. Mol. wt. found: 136.

The Oxidation.—When ferric chloride was added to an aqueous solution of m-xylorcinol, a momentary blue color was followed by a turbidity which increased until a voluminous precipitate had settled out. The precipitate was very sparingly soluble in water, for a 0.01% solution of m-xylorcinol gave a distinct turbidity when a drop of ferric chloride was added, although the first blue color was not visible with so dilute

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[8] Maltese and Errera, *Gazz.* chim. *ital.*, II, **33,** 277 (1903).

[9] Pfaff, *Ber.*, 16, 616, 1136 (1883).

a solution. The precipitate had an olive-green color, evidently due to accidental traces of iron. Two samples, thoroughly washed and dried, contained, respectively, 0.24 and 0.56% of iron. The compound which might be formed from one atom of iron and three molecules of m-xylorcinol would contain 12% of the metal. By repeatedly dissolving in benzene and precipitating with ligroin, the pure substance was obtained as a faintly yellow amorphous powder which contained no iron. The aqueous filtrate from the original precipitate reduced many times as much permanganate as corresponded to the total possible ferrous chloride, a fact which suggested that it contained either m-xylorcinol or some water-soluble oxidation product of that substance. Extraction with ether gave di-m-xylorcinol. When an aqueous solution of this substance was treated with ferric chloride, it yielded the familiar olive-green precipitate.

Experiments in which known amounts of *m*-xylorcinol were treated in aqueous solution at laboratory temperature with ferric chloride in slight excess showed that the first product of the oxidation, the water-soluble di-m-xylorcinol, was formed rapidly but oxidized slowly and gradually decreased in amount, while the amorphous insoluble product of the further oxidation increased in amount as the solution was allowed to stand. Titration of an aqueous solution of m-xylorcinol with standard ferric chloride solution, ammonium thiocyanate on a spot plate being used as an indicator, showed that the reaction took place in two stages. The ferric chloride was at first reduced almost instantly until a fairly sharp change of rate occurred, after which the reduction proceeded slowly until finally no more ferric chloride was reduced. A fairly good end-point could be measured for the first stage of the reaction and was found to correspond to one molecule of ferric chloride per molecule of m-xylorcinol, 0.533 g. of m-xylorcinol (0.0039 mole) consuming 23 cc. of 0.16 M ferric chloride solution (0.0037 mole). The end-point, however, did not represent an abrupt boundary between the two stages of the oxidation, for a small amount of precipitate had already formed and a corresponding small amount of m-xylorcinol evidently remained unoxidized.

Since di-m-xylorcinol, the first product of the oxidation, was found to be soluble in ether as well as in water, it was hoped that it might be obtained in better yield if the oxidation was carried out in the presence of ether, by which it would be taken up and removed from the influence of the oxidizing agent. The expectation was verified. Ether solutions of m-xylorcinol were shaken in the shaking machine with aqueous solutions of ferric chloride in large excess, and after a known time interval the ether phase was removed and worked up for di-m-xylorcinol. Results were as shown in Table I.

TABLE I

TWO-PHASE OXIDATION, EFFECT OF TIME AND CONCENTRATION

m-Xylorcinol, g.	Ether, cc.	Ferric chloride, cc. 1 N	Time, hours	Di-*m*-xylorcinol, weight per cent.
1.000	150	100	2	32.9
1.000	150	100	2.5	35.5
1.000	150	100	3	34.0
0.619	200	50	2	17.6
.619	200	50	6	30.2
.502	50	50	1	33.0

The first three experiments show that the yield of di-m-xylorcinol increases with increasing duration of shaking until it drops off again after a maximum has been reached. The series shows that the best yields are probably to be obtained by the long shaking of dilute solutions.

In one experiment 0.533 g. of m-xylorcinol yielded 0.200 g. of di-m-xylorcinol and 0.326 g. of the amorphous oxidation product, a total of 0.526 g. or very nearly the weight of the original material which was oxidized.

Di-*m*-xylorcinol.—The ether solution from the two-phase oxidation was evaporated just to dryness and the residue, recrystallized from benzene, yielded colorless needles of di-m-xylorcinol, m. p. 242–243° with slight decomposition. The first mother liquors contained traces of m-xylorcinol and a small quantity of the amorphous oxidation product. Di-*m*-xylorcinol is much less soluble in water than m-xylorcinol. It is practically insoluble in cold benzene, but about 0.93 g. dissolves in 100 cc. of the boiling solvent. Small quantities were sublimed unchanged both at reduced and at atmospheric pressure. When distilled with zinc dust it yielded a substance which had an odor resembling that of diphenyl, and melted at 81–94", but was too small in amount for further examination. A chloroform solution of this material, which was evidently dixylyl, gave a violet coloration when poured upon a fresh sublimate of aluminum chloride.

Anal. Subs., 40.23, 40.95 mg.: CO_2, 104.19, 105.44 mg.; H_2O, 24.24, 24.43 mg. Calcd. for $C_{16}H_{18}O_4$: C, 70.04; H, 6.62. Found: C, 70.66, 70.24; H, 6.47, 6.68.

Molecular Weight. Subs., 0.0115, 0.0124 g.; camphor, 0.1045, 0.1161 g.; AT, 17.4°, 21.2°. Calcd. for $C_{16}H_{18}O_4$: 274. Found: 252, 249.

Di-m-xylorcinol tetra-acetate was prepared by refluxing di-m-xylorcinol with acetic anhydride and anhydrous sodium acetate, as colorless crystals from ligroin, m. p. 158–159°. It was not soluble in warm caustic soda solution, and was recovered unchanged after refluxing for several minutes with a chloroform solution of a large excess of bromine. It gave no color with ferric chloride solution.

Anal. Subs., 41.52, 33.18, 36.84 mg.: CO_2, 99 26, 79.38, 87.96 mg.; H_2O, 21.75, 17.52, mg. Calcd. for $C_{24}H_{26}O_8$: C, 64.99; H, 5.91. Found: C, 65.22, 65.27, 65.14; H, 5.86, 5.91.

Molecular Weight. Subs., 0.0241, 0.0211 g.; camphor, 0.1103, 0.0776 g.; AT, 20.7°, 24.5". Calcd. for $C_{24}H_{26}O_8$: 443. Found: 421, 431.

The Amorphous Oxidation Product, Probably Di-(di-m-xylorcinol) Ether.—This substance was prepared by adding an excess of ferric chloride to an aqueous solution of m-xylorcinol and allowing it to stand until precipitation was complete. The greenish precipitate, after washing and drying, was purified by repeatedly dissolving in benzene and precipitating with ligroin, and yielded the pure material in the form of a pale yellow amorphous powder which charred gradually when heated above 250". It dissolved readily in caustic alkali solution and was reprecipitated by acid. It reduced ammoniacal silver nitrate and did not liberate iodine from a solution of potassium iodide acidified with hydrochloric acid. It dissolved readily in benzene, chloroform, alcohol and ether, but was insoluble in cold ligroin and petroleum ether.

Anal. Subs., 38.81, 37.31 mg.: CO_2, 97.56, 93.64 mg.; H_2O, 20.87, 20.10 mg. Calcd. for $C_{32}H_{34}O_9$: C, 68.30; H, 6.09. Found: C, 68.58, 68.47; H, 6.02, 6.04.

Molecular Weight. Subs., 0.0186, 0.0109 g.; camphor, 0.1161, 0.0514 g.; AT, 12.6°, 16.0". Calcd. for $C_{32}H_{34}O_9$: 563. Found: 505, 530.

Bromination of *m*-**Xylorcinol.**—Two grams of m-xylorcinol was dissolved in 100 cc. of chloroform, 2.32 g. of bromine in 40 cc. of chloroform added and the mixture refluxed for an hour, at the end of which time hydrogen bromide was no longer given off. The residue from the evaporation was purified by sublimation at 110° and 1 mm. and yielded pure monobromo-*m*-xylorcinol in almost theoretical amount as colorless needles, m. p. 119–119.5". An excess of bromine was found to reduce the yield.

When bromine was added to a chloroform solution of monobromo-m-xylorcinol, hydrogen bromide was given off and a reddish-brown solution resulted which yielded a brown amorphous powder on evaporation. In one experiment, where a large excess of bromine was used, small dark blue crystals were deposited on the walls of the test-tube. These were too small in amount for further study but were notable because of their similarity in appearance to a substance which was produced by the action of an excess of bromine on di-m-xylorcinol.

Aqueous solutions of m-xylorcinol and of monobromo-m-xylorcinol both decolorized bromine water with the production of a white precipitate; both substances yielded the same products with an excess of bromine water. We have isolated three crystalline substances from the white precipitate, but all in insufficient quantity for analysis. They melted, respectively, at *71–72, 173* and 194°, and all decomposed above the melting point, giving off large quantities of gas in which bromine was detected by iodo–starch paper. The first, m. p. *71–72'*, liberated **iodine** from acidified alcoholic potassium iodide; the others did not.

Oxidation of Monobromo-*m*-xylorcinol.—The white precipitate produced by the action of an excess of ferric bromide on an aqueous solution of monobromo-m-xylorcinol was found to contain an amorphous substance, m. p. 128–135°, and a crystalline material, insoluble in water, sparingly soluble in cold benzene but readily in hot, as small faintly yellowish needles which did not melt but charred gradually between *265* and *278".* The yield of the crystalline product was *26.2–26.5%* of the weight of the original monobromo-*m*-xylorcinol.

Anal. Subs., *22.86, 25.12* mg.: CO_2, 41.43, 45.71 mg.; H_2O, *7.95, 8.57* mg. Subs., *18.98, 19.03* mg.: AgBr, *14.59, 14.50* mg. Found: C, *49.44, 49.64;* H, *3.89, 3.82;* Br, *32.40, 32.67.*

Molecular Weight. Subs., *0.0135, 0.0139, 0.0078 g.;* camphor, *0.1053, 0.0715,* 0.0541 g.; ΔT, 9.6°, 16.1°, 11.6°. Found: *531,480,497.*

If the substance contains one bromine atom, the molecular weight calculated from the found percentage of bromine would be *246;* if two atoms of bromine, *492;* if three, *738.* We conclude then that it contains two bromine atoms, but the corresponding calculated empirical formula, $C_{20}H_{19}Br_2O_4$ (corresponding to carbon 49.70%, hydrogen 3.96%, bromine 33.08%, and molecular weight 483.1), does not appear to represent any probable oxidation product of monobromo-m-xylorcinol.

Bromination of Di-*m*-xylorcinol.—When di-m-xylorcinol was treated with two moles of bromine in chloroform solution, there was no apparent action at room temperature, but hydrogen bromide was given off on boiling and, after a few minutes, fine silky colorless crystals appeared in the liquid. The solution was chilled and the crystals removed. The chloroform mother liquors were reddish colored and on evaporation gave a small amount of dark blue crystals. The colorless needle crystals, recrystallized from benzene, melted with decomposition at *274–277'* and amounted to 29–30% of the weight of the original di-m-xylorcinol. The simple introduction of two bromine atoms into di-m-xylorcinol would produce *161* weight per cent. of product. Analysis and molecular weight determinations gave results which correspond fairly closely to di-*m*-xylorcinol in which two of the hydroxyl groups have been replaced by bromine atoms.

Anal. Subs., 27.13, 23.29 mg.: CO_2, 46.96, 40.28 mg.; H_2O, 9.70, 7.06 mg. Subs., *18.65, 9.54* mg.: AgBr, *14.21,* 8.66 mg. Calcd. for $C_{16}H_{16}O_2Br_2$: C, *48.01;* H, *4.03;* Br, *39.95.* Found: C, *47.22, 47.18; H, 4.00, 3.39;* Br, 39.25, 38.63.

Molecular Weight. Subs., *14.21, 10.96* mg.: camphor, *63.26, 63.21* mg.; *AT,* 20.8°, 17.7°. Calcd. for $C_{16}H_{16}O_2Br_2$: 400. Found: 429,896.

Summary

m-Xylorcinol (4,6-dihydroxyxylene-1,3), when oxidized with ferric chloride in aqueous solution, first yields di-m-xylorcinol in which the two nuclei are evidently joined through the position between the hydroxyl groups. **The** further action of ferric chloride converts di-m-xylorcinol into an

insoluble amorphous tetranuclear substance which is probably di-(di-m-xylorcinol) ether.

The action of bromine on m-xylorcinol, on monobromo-m-xylorcinol and on di-m-xylorcinol, and the oxidation of monobromo-m-xylorcinol by means of ferric bromide in aqueous solutions have also been investigated.

CAMBRIDGE, MASSACHUSETTS

(CONTRIBUTION NO. 186 FROM THE DEPARTMENT OF CHEMISTRY, UNIVBRSITY OF PITTSBURGH]

SYNTHETIC GLYCERIDES. II. REFRACTIVE INDICES OF GLYCERIDES OF KNOWN CONSTITUTION

BY H. P. AVERILL, J. N. ROCHE AND C. G. KING

RECEIVED JULY 31, 1929 PUBLISHED JANUARY 8, 1930

In a previous paper,[1] methods for the synthesis of symmetrical and unsymmetrical triglycerides containing two fatty acids were given in detail and data for their melting points were included. It was pointed out that the melting point of the symmetrical isomer in each of the sets of isomeric triglycerides made was slightly higher than that of the unsymmetrical isomer. In continuing a study of the relation between their molecular structure and physical properties, a study of the refractive indices of these isomers has been made.

Although the refractive index is one of the most widely used physical constants for the identification of natural glycerides (oils and fats), very little is known of the relation of this property to the constitution of the component glycerides. Furthermore, as stated by Myddleton and Barry,[2] "at present it is not known whether the refractive index of a mixed triglyceride is the same as the corresponding mixture of simple glycerides." In this paper data are also given for the comparison of three sets of isomers with equivalent mixtures of the corresponding simple triglyeerides.

It was expected that any differences in the refractive indices of the isomers would be small. Apparatus was, therefore, devised by means of which a constant temperature could be held for a considerable length of time and which permitted the use of an immersion refractometer.

Apparatus.—The constant temperature bath was a round three-liter flask with the original neck shortened and three other necks, each one inch in diameter. These contained, respectively, the immersion refractometer, leads for the heating element, a standardized thermometer and a Liebig condenser.

A Zeiss immersion refractometer was used, fitted with an auxiliary prism and a metal beaker. The metal beaker made the enclosed sample air and water tight. As

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[1] H. P. Averill, J. N. Roche and C. G. King, THIS JOURNAL, 51, 866 (1929).

[2] W. W. Myddleton and T. H. Barry, "Fats, Natural and Synthetic," Ernest Benn, Ltd., London, 1924, p. 93.

a further precaution a glass tip was placed over the end of the metal beaker and held in place by a tightly fitting rubber stopper protected with tin foil This stopper was about three-eighth of an inch thick, allowing uniform heating of the prisms and an uninterrupted transmission of heat into the metal case. Another rubber stopper in the shoulder of the flask held the refractometer in place. The lower end of the condenser was beveled so that the condensate could not form a seal and thus vary the pressure inside the flask. The whole apparatus was supported on a cork ring and held by a similar ring on top.

One degree variation in temperature would change the refractive index approximately 4 in the fourth place. By means of the vapor-bath it was possible to hold the temperature constant within ±0.02° as long as desired. By using liquids such as acetone, methyl alcohol and ethyl alcohol, the temperature inside the bath reached a maximum within five or six minutes, and thereafter remained practically constant. Several runs were recorded in which the temperature did not vary more than 0.01" during thirty minutes. By the use of sodium light the border line was sharp and could be checked repeatedly to ±0.02 scale divisions, which is equivalent to ±5 in the sixth place for the index of refraction.

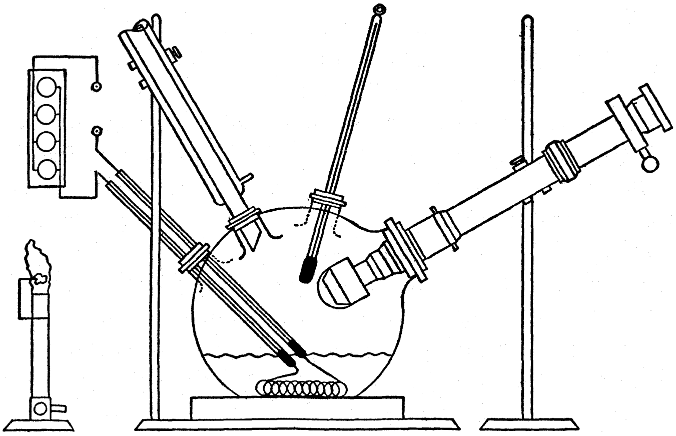


Fig. 1.—Constant temperature bath for refractometer.

Measurement of Refractive **Indices.**—Since there is some question as to the stability of a triglyceride when kept even at room temperature, the refractive indices were measured within a few days from the date of final crystallization. To remove any final traces of solvent, the crystalline compounds, already very dry, were placed in a vacuum desiccator at 40° and subjected to a vacuum of 8 mm. for a period of several hours. They were then carefully melted over a hot-plate and a few drops applied to the warm prisms. The metal beaker was then put in place and the refractometer inserted into the bath as shown in the accompanying diagram.

The values given in Table I for exact temperatures were obtained from readings near these points, corrected to the exact temperatures by use of the dn/dt factors obtained from a series of readings near those temperatures.

Discussion of Results.—It is evident from the data given in Table I that the symmetrical mixed triglycerides are characertized by a higher

TABLE I

REFRACTIVE INDICES

Compound	Refr. *index at* 70°	Refr. *index at* 75°
β-Stearodilaurin	1.44031	1.43850
or-Stearodilaurin	1.43986	1.43789
Equiv. mixture of simple triglycerides	1.44036	1.43859
β-Stearodipalmitin	1.44325	1.44160
or-Stearodipalmitin	1.44289	1.44115
Equiv. mixture of simple triglycerides	1.44289	1.44112
β-Laurodimyristin	1.43901	1.43719
a-Laurodimyristin	1.43798	1.43548
Equiv. mixture of simple triglycerides	1.43847	1.43661
β-Laurodipalmitin	1.44044	1.43830
α-Laurodipalmitin	1.44016	1.43789
β-Acetodipalmitin	1.43749	1.43567
or-Acetodipalmitin	1.43709	1.43526

Average dn/dt for five symmetrical isomers, 0.00037
Average dn/dt for five unsymmetrical isomers, 0.00039
Average dn/dt for three mixtures of simple triglycerides, 0.00036

index of refraction than that of their unsymmetrical isomers (average difference for five sets of isomers, 0.00062 at 75').

The index of refraction of equivalent mixtures of simple triglycerides may be expected to fall closely within the range covered by the respective isomers. From the constancy of readings over a period of an hour or more at 75°, it is evident that-the isomeric mixed triglycerides are comparatively stable at this temperature when isolated in pure form.

Summary

Apparatus was devised for using an immersion refractometer in a constant temperature bath at a range of 65–78'. The refractive indices of five sets of isomeric mixed triglycerides (two fatty acids) have been determined at 70 and 75°. In each case the symmetrical isomer had the higher value, the average difference being 0.00062 at 75°. The average dn/dt values over this temperature range are also given. Equivalent mixtures of simple triglycerides gave values lying within the range of the corresponding isomeric triglycerides.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE INSTITUTE OF PHYSIOLOGY OF NUTRITION OF MOSCOW]

THE SYNTHESIS OF DIMETHOXYPHTHALIMIDINE-ACETIC ACID

BY W. M. RODIONOW AND A. M. FEDOROVA

RECEIVED AUGUST 2, 1929 PUBLISHED JANUARY 8, 1930

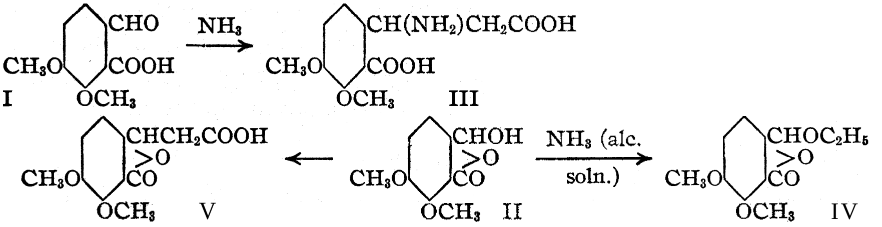
Some time ago[1] we announced a general method for the preparation of aryl-β-amino fatty acids by the condensation of aromatic aldehydes with malonic acid according to the equation

$$\mathrm{RCHO + NH_3 + CH_2(COOH)_2 = RCH(NH_2)CH_2COOH + CO_2 + H_2O}$$

The mechanism of this reaction was explained in the paper with E. A. Postovskaja[1d] as a condensation reaction between aldehyde-ammonia and malonic acid

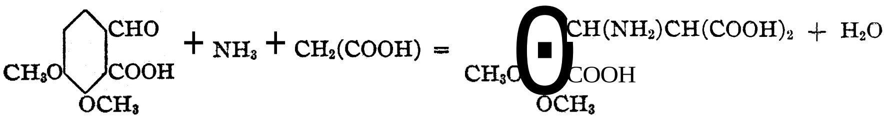
$$\mathrm{RCH(OH)NH_2 + CH_2(COOH)_2 = RCH(NH_2)CH_2COOH + CO_2 + H_2O}$$

It was very interesting for many reasons to extend this reaction to an aldehyde carbonic acid. We have chosen for this purpose the most accessible substance of this type, opianic acid. This substance can react in two forms, as a true aldehyde, I, or in its ψ-form as an alcohol, II



Only the first form could give 3′,4′-dimethoxyphenyl-1′-β-alanine-2′-carbonic acid, III; the second form would give the #-ethyl ester of opianic acid, IV, and meconine-acetic acid, V.

Experiment showed that the condensation with opianic acid gave a mixture of the corresponding amino acid and meconine-acetic acid; the formation of the ψ-ethyl ester was not established. It is possible that this condensation takes place in the same course, as we have shown with benzaldehyde and piperonal[1e]



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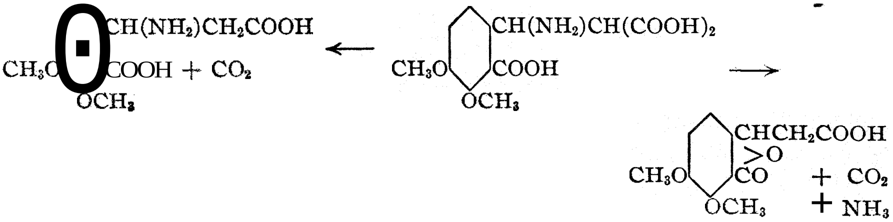
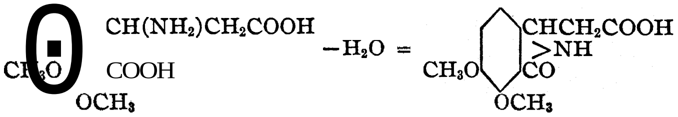
[1] (a) W. M. Rodionow and E. Th. Malevinskaja, Ber., 59, 2952 (1926); (b) W. M. Rodionow and A. M. Fedorova, *ibid.*, **60**, 804 (1927); (c) *Arch. Pharm.*, **266**, 116–121 (1928); (d) W. M. Rodionow and E. A. Postovskaja, THIS JOURNAL, 51, 841 (1929); (e) W. M. Rodionow, *ibid.*, 51, 847 (1929).



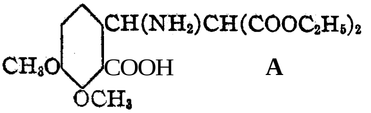
Until now we have not succeeded in isolating the tricarbonic acid and have obtained only the β-aryl-amino acid and meconine-acetic acid. The method of preparation of these substances is a very simple process. Equimolecular proportions of opianic and malonic acids and a slight excess of alcoholic ammonia solution are heated for two to three hours, then dissolved in soda solution, filtered off from small quantities of resinous matter and acidified. The precipitated mixture of both acids is separated with ether (see Experimental Part). The purified dimethoxyphenylalanine-carbonic acid melts over the range of 134–137° uncorr. Further crystallization from alcohol slowly changed the melting point; it became higher and nitrogen determinations gave larger percentages of nitrogen.

It seemed very probable that this acid would give a phthalimide derivative easily (with ring formation and loss of water) in accordance with the equation

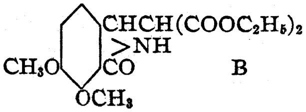


This supposition was proved experimentally. On heating the amino acid above its melting point for one to two hours, evolution of water takes place and the phthalimidine derivative is formed nearly quantitatively. When recrystallized from alcohol this substance melts at 174–175° and gives without difficulty a methyl ester and a nitrosamine derivative.

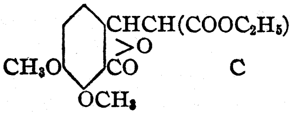
In our former investigation[1b] we showed that by replacing malonic acid by its ester, one could obtain the ester of β-aryl-β-amino-isosuccinic acid. It was expected that in the case of opianic acid either the derivative with the open chain, opianylmalonic ester (A) or the corresponding phthalimidine derivative (B) would be obtained. Both esters might be accompanied by the meconine-malonic ester (C).



A



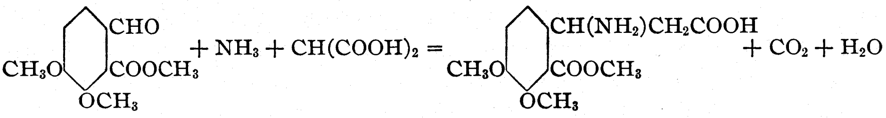
B



C

Our attempts to prepare these substances showed that only the meconine-malonic ester, not yet described, was obtained. It is a new confirmation of our former investigations, that the formation of esters of the β-aryl-β-amino-isosuccinic acid does not go with such good yield as the preparation of β-phenylalanine derivatives.

In order to avoid the ring formation we tried to condense the true esters (a-esters) of opianic acid with malonic acid in accordance with the equation



We have found, however, that methyl alcohol is split off and dimethoxyphthalimidine-acetic acid is formed exclusively.

Experimental Part

p-3′,4′-Dimethoxy-2′-carboxyphenyl-1′-β-aminopropionic Acid, $(CH_3O)_2C_6H_2(COOH)CH(NH_2)CH_2(COOH)$.—A mixture of 20 g. of opianic acid, 40 cc. of 10% alcoholic ammonia solution and 10 g. of malonic acid is heated for two hours on a boiling water-bath with a condenser set for distillation. The condensation product is dissolved in 10% soda solution, filtered from small quantities of tarry matter and acidified with hydrochloric acid. A heavy oil begins to separate from the solution and solidifies very slowly, but it is not advisable to allow it to crystallize as it is much more difficult to purify the solid substance. The acidified mixture of oil and water is immediately shaken with a large quantity of ether, whereby only the meconine-acetic acid goes into solution in the ether layer and gives, after recovery and recrystallization from water, 7.8 g. of substance melting at 165–167°. The yield is about 32.7% of the theoretical amount.

From the water solution the amino acid crystallizes after standing. Complete separation requires from ten to twelve hours, but the time is diminished considerably if mechanical stirring is used. The yield is 13.2 g. (about 55% of the theoretical). The filtrate gives after evaporation 3 g. of heavy oil, a mixture of opianic, meconine-acetic and β-amino acids.

The pure dimethoxyphenylalanine-carbonic acid crystallizes in thin plates from alcohol, is soluble in water and insoluble in ether. It melts at 132–134° with loss of water.

Anal. Calcd. for $C_{12}H_{15}O_6N$: N, 5.21. Found: N, 5.23, 5.28.

3,4-Dimethoxyphthalimidine-acetic Acid.—Three grams of dimethoxyphenylalanine-carbonic acid is heated for two hours on an oil-bath at 140–150°. The substance remaining is recrystallized from alcohol and then melts at 174–175°.

Anal. Calcd. for $C_{12}H_{13}O_5N$: N, 5.57. Found: N, 5.5, 5.6.

Methyl Dimethoxyphthalimidine-acetate, $(CH_3O)_2\overline{C_6H_2CONHC}HCOOCH_3$.—Two grams of dimethoxyphthalimidine-carbonic acid is dissolved in methyl alcohol and a current of dry hydrogen chloride is passed into the solution. This requires about two hours. After saturation the mixture is heated for two hours on the water-bath. When the temperature has dropped to 20–25°, the solution is poured into water and the substance which separates is filtered off and dried. The yield is 1.65 g. (about 80% of the theoretical). On recrystallizing from alcohol the ester gives lustrous prisms melting at 141–143°. The substance is easily soluble in alcohol and ether and is insoluble in water.

Anal. Calcd. for $C_{13}H_{15}O_5N$: N, 5.28. Found: N, 5.30.

Preparation of the Nitrosamine of Dimethoxyphthalimidine-carbonic Acid.—Two grams of dimethoxyphthalimidine-carbonic acid is dissolved in 40 cc. of water and mixed with 15 cc. of concd. hydrochloric acid. The solution is cooled with ice and treated little by little with 7 cc. of 10% sodium nitrite solution. After stirring for some time, the precipitated nitrosamine derivative is filtered by suction and crystallized from water. The yield is 1.9 g. (about 90% of the theoretical). The pure product melts at 167° with decomposition; it may be titrated with sodium hydroxide. Neutralization of 0.2 g. of the substance required 7.14 cc. of 0.1 *N* sodium hydroxide.

3,4-Dimethoxyphthalimidine-acetic acid from the α-Methyl Ester of Opianic Acid.—Two and one-half grams of α-ester and 1.2 g. of malonic acid are mixed with 5 cc. of 10% ammonia solution and heated for two hours on a boiling water-bath. The condensation product is dissolved in 10% soda solution and filtered. The filtrate is acidified with hydrochloric acid. The precipitate after crystallization from alcohol melts at 172–174". The yield is 1.7 g. (about 60% of the theoretical). The melting point of this substance mixed with the dimethoxyphthalimidine-acetic acid of other preparations did not show any depression.

Diethyl Meconine-malonate, $(CH_3O)_2\overline{C_6H_2COOC}HCH(COOC_2H_5)_2$.—A mixture of 20 g. of opianic acid, 15.3 g. of malonic ester and 25 cc. of 14% alcoholic ammonia solution is heated as usual for five hours. The condensation product, a heavy oil, is dissolved in ether and separated from a part of the oil which is not soluble in ether. The ethereal solution is treated with an alcoholic solution of hydrogen chloride and filtered again. The ether solution is then evaporated on the water-bath to a small volume. On cooling the diethyl meconine-malonate separates in large white prisms. The yield of unpurified substance is 26.5 g. (about 75% of the theoretical.) The product is very easily soluble in ether or alcohol and insoluble in water. The diethyl meconine-malonate melts at 74–75° after recrystallization from alcohol.

Anal. Subs., 0.1300: CO_2, 0.2756; H_2O, 0.0673. Calcd. for $C_{17}H_{20}O_8$: C, 57.95; H, 5.68. Found: C, 57.82; H, 5.75.

Summary

The reaction between opianic acid and malonic acid in the presence of alcoholic ammonia solution has been investigated and it was found that the primary condensation product, the β-phenylalanine derivative, forms dimethoxyphthalimidine-aceticacid very easily on heating, and that the condensation of opianic acid with malonic ester does not give an amino derivative but results in the corresponding meconine-malonic ester. The preparation and properties of these compounds are described.

Moscow, U. S. S. R.

[Contribution from the Chemical Laboratory of Brown University]

STUDIES RELATING TO ORGANIC GERMANIUM DERIVATIVES. II. SOME TRIPHENYL GERMANIUM DERIVATIVES AND THEIR REACTIONS

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In the development of the chemistry of germanium, certain simple triphenyl germanium derivatives have been prepared and some of their reactions have been studied. A comparison of the properties of such compounds with those of corresponding compounds of carbon presents interesting contrasts. Thus triphenyl germanium amine is extremely susceptible to hydrolysis, while the analogous organic amines are comparatively stable. Triphenyl germanium amine results from the action of gaseous ammonia upon solutions of triphenyl germanium bromide or other halides in organic solvents. The product is so sensitive toward moisture that it is largely hydrolyzed in the operations incident to its separation unless extreme precautions are taken. Even then this method does not serve in preparing a strictly pure compound.

Since the amine upon hydrolysis yields triphenyl germanium oxide and ammonia, the process, as a whole, is expressed by the equations

$$(C_6H_5)_3GeBr + 2NH_3 = NH_4Br + (C_6H_5)_3GeNH_2 \quad (1)$$
$$2(C_6H_5)_3GeNH_2 + H_2O = 2NH_3 + [(C_6H_5)_3Ge]_2O \quad (2)$$

Triphenyl germanium amine may also be prepared by the action of potassium amide on triphenyl germanium bromide in ammonia solution. In this case, reaction is facilitated by an excess of potassium amide, which forms a monopotassium salt of the amine. This behavior is similar to that of the simpler aromatic amines;[1] triphenylmethylamine, however, does not react with potassium amide.[2] The following equations represent the reactions

$$(C_6H_5)_3GeBr + KNH_2 = (C_6H_5)_3GeNH_2 + KBr \quad (3)$$
$$(C_6H_5)_3GeNH_2 + KNH_2 = (C_6H_5)_3GeNHK + NH_3 \quad (4)$$

The amine may be liberated from its salt by means of ammonium bromide. It appears as a fine white crystalline precipitate. The following reaction is involved

$$(C_6H_5)_3GeNHK + NH_4Br = KBr + NH_3 + (C_6H_5)_3GeNH_2 \quad (5)$$

The amine is further distinguished from its organic analogs by its marked tendency to lose ammonia with the formation of the imine, $[(C_6H_5)_3Ge]_2NH$. This sometimes occurs immediately upon precipitation. Attempts to recrystallize the amine invariably yielded mixtures of triphenyl germanium amine and imine and, perhaps, also the nitride.

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[1] White, Morrison and Anderson, This Journal, 46,967 (1924).

[2] Kraus and Rosen, *ibid.*, 47,2739 (1925).

This tendency of the amine to lose ammonia is paralleled by that of the corresponding hydroxide, triphenyl germanol, to lose water. On hydrolyzing triphenyl germanium halides, the oxide is invariably obtained. Kraus and Foster[3] have shown that the germanol may be obtained indirectly from sodium triphenyl germanide by oxidation of this salt to the germanolate and subsequent hydrolysis of this compound. Although triphenyl germanol loses water at higher temperatures, it is comparatively stable under ordinary conditions, much more so, in fact, than the corresponding amine.

Complete conversion of the amide to the nitride may be effected by heating the primary amine above 200° under atmospheric pressure and then evacuating the containing tube. The nitride may be purified by fractional sublimation in *vacuo* or by recrystallization from dry petroleum ether. From the latter solvent it crystallizes in colorless needles which melt at 163–164° (corr.).

Analysis of the amine was first carried out by decomposing the compound with hydrochloric acid and separating the ammonium chloride from the triphenyl germanium chloride[4] formed in this reaction. The latter compound, which was also prepared from the oxide, was found to melt at 116° (corr.). It is interesting to note that neither a nitrate nor a sulfate could be prepared by a similar method. The triphenyl germanium oxide was recovered unchanged, showing that it is much more resistant to hydrolysis than its structural analog, bis-triphenylmethyl ether.[5] The oxide is readily attacked by sodium in liquid ammonia solution. Apparently the primary products of this reaction are sodium triphenyl germanide, $(C_6H_5)_3GeNa$, and sodium triphenyl germanolate, $(C_6H_5)_3GeONa$. These products are analogous to those obtained by the cleavage of aromatic ethers with sodium–potassium alloy.[6]

It is evident that the compounds of germanium with electronegative elements show a somewhat greater reactivity than do their carbon analogs.

Experimental Part

Action of Ammonia on Triphenyl Germanium Bromide.—Triphenyl germanium bromide was treated with liquid ammonia at its boiling point, −33.5°. Solutions of triphenyl germanium bromide in ether, petroleum ether and benzene were also treated with gaseous ammonia at ordinary temperatures. The reactions were carried out in tubes similar to those described by White[7] but ground-glass joints were employed throughout in place of rubber stoppers and inlet and outlet tubes were provided with

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[3] Kraus and Foster, This Journal, 49,457 (1927).

[4] Subsequent to the completion of the present investigation, Orndorff, Tabern and Dennis, *ibid.*, 49, 2513 (1927), have reported the preparation of the chloride by a similar method. They give its melting point as 117–118°.

[5] Gomberg, *ibid.*, 35, 200 (1913); *Ber.*, 46,225 (1913).

[6] Ziegler and Thielmann, *ibid.*, 56, 1740 (1923).

[7] White, This Journal, 45, 779 (1923).

stopcocks so that the tube could readily be evacuated. The entire tube length was **40** cm. and it could be weighed on a 2-kilo balance.

When ammonia was passed through a solution of triphenyl germanium bromide in an organic solvent, a precipitate was formed immediately which, upon separation and analysis, proved to be ammonium bromide.

Anal. Subs., **0.2970, 0.3959:** AgBr, **0.5694, 0.7527.** NH_4Br recovered, **100.14,** 99.11%.

The organic residue was soluble in benzene and was crystallized therefrom and identified as triphenyl germanium oxide, m. p. 183–184° (corr.).[8]

The molecular weight of the oxide was determined in benzene at **its** boiling point by a modification of the Cottrell[9] method.

Mol. wt. Solvent, **32.57, 31.55;** solute, **1.370, 2.197;** At, 0.183°, 0.302'. **Calcd.** for $[(C_6H_5)_3Ge]_2$: mol. wt., **623.4.** Found: **620.6, 622.6,** mean, **621.6.**

The molecular weight of the oxide in benzene appears to be normal.

On treating the bromide with liquid ammonia, some unchanged triphenyl germanium bromide was usually recovered at the end of the experiment. The amount of ammonia absorbed in the reaction, as determined by weight increase, varied from **1.72** to **1.96** moles per mole of bromide. This indicates the preliminary formation of triphenyl germanium amine, but it was found impossible to obtain both a complete reaction and an oxide-free product.

Action of Potassium Amide on **Triphenyl** Germanium Bromide **in** Liquid Ammonia. **—A** quantity of metallic potassium more than equivalent to the triphenyl germanium bromide to be treated was converted to potassium amide in liquid ammonia solution by means of a bit of rusty iron as a catalyst. This catalyst was removed when the reaction was complete. The ammonia was then evaporated and the reaction tube evacuated. The tube was next filled with pure dry nitrogen and triphenyl germanium bromide **(1.302** g.) was introduced. This procedure was necessary, since ammonia vapor causes the bromide to cake on the walls of the reaction tube. The nitrogen was removed by means of a pump and ammonia was condensed on the materials in the tube. Reaction took place at once. It was accompanied by a decrease in the weight of the non-volatile contents of the tube amounting to **0.0605** g., which is equivalent to **1.113** moles of ammonia per mole of the original bromide used. The ammonia used in this reaction was dried by means of sodium in an auxiliary tube; the reaction tube was pre-dried by heating to **200'.**

The product obtained under these conditions was completely soluble in liquid ammonia and insoluble in ether. Upon hydrolysis the product became partially soluble in petroleum ether. When ammonium bromide was added equivalent to the excess of potassium amide, a precipitate was formed in the liquid ammonia solution. After evaporating the ammonia and exhausting the reaction tube, the gain in weight in two experiments corresponded to **15.42** and **16.92** g. per mole of the original bromide, **while** **16.00** g. is required for the formation of the amine, $(C_6H_5)_3GeNH_2$. Evidently triphenyl germanium bromide reacts with potassium amide according to Equation **3.**

The amount of free potassium amide was approximated by titrating the solution with ammonium bromide until a permanent precipitate began to appear. In two experiments the amount of potassium amide reacting with the bromide was found to be **1.842** and **1.879** moles, respectively. For the formation of the monopotassium salt two

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[8] This oxide separates from benzene in the form of characteristic crystals containing two molecules of solvent which are slowly lost upon standing in the air at ordinary temperature. The benzene may be removed readily by heating the compound to **100°** in an oven.

[9] **Cottrell, THIS JOURNAL,** 41, **721 (1919).**

moles of potassium amide is required. The method of titration is not a precise one, since it is possible that the amine is appreciably soluble in liquid ammonia.

Triphenyl Germanium Nitride.—In order to obtain the amine, or its de-ammoniation products, in a pure state, reactions were carried out in a two-legged tube, which permitted the recrystallization of the products of reaction from petroleum ether in absence of air and moisture. When the initial reaction was completed, the ammonia was evaporated, the tube exhausted and petroleum ether introduced. The organic residue, being soluble in the ether, was decanted into the second leg, after which the solvent was recondensed in the first leg and the process repeated until the organic material was completely separated from the inorganic salts. Analysis of the product indicated that the amine lost ammonia during recrystallization. Accordingly, in later experiments, the product was heated to 200° and the tube was evacuated to facilitate the loss of ammonia. Under these conditions the product sublimed to the colder parts of the tube immediately above the bath. These crystals were then analyzed for nitrogen by dissolving in warm alcohol acidified with hydrochloric acid. The resulting solution was diluted with water and separated from precipitated triphenyl germanium chloride by filtration. Sodium hydroxide was added to the filtrate to liberate the ammonia, which was distilled and titrated with standard acid.

Anal. Subs., 0.3535, 0.6040, 0.3063: cc. of 0.0999 N HCl, 3.78, 7.28, 3.48. Calcd. for $[(C_6H_5)_3Ge]_3N$: N, 1.98. Found: N, 1.82, 2.05, 1.93; mean, 1.94.

Action of Sodium on Triphenyl Germanium Oxide in Liquid Ammonia.—A known weight of triphenyl germanium oxide was treated with metallic sodium in liquid ammonia. The first two equivalents of sodium, which were added slowly, reacted fairly rapidly. Thereafter reaction was quite slow and the reaction mixture was left for fifteen hours with a considerable excess of metal. At the end of that time the free metal was titrated back with ammonium bromide until the blue color, due to sodium, just disappeared. The solution exhibited a yellow color and a considerable quantity of a white precipitate was present. The yellow color was doubtless due to sodium triphenyl germanide, while the precipitate was taken to be sodium triphenyl germanolate. In three experiments, 2.42, 2.60 and 2.46 equivalents of metal reacted per mole of triphenyl germanium oxide. It was inferred that reaction takes place as follows

$$[(C_6H_5)_3Ge]_2O + 2Na = (C_6H_5)_3GeNa + (C_6H_5)_3GeONa \qquad (6)$$

While the sodium is capable of breaking down readily the first of the germanium–oxygen bonds, it attacks the second only with difficulty if at all. If the second bond had been completely broken down, four atoms of sodium should have been used up in the reaction.

The values found for the amount of sodium used are somewhat higher than required according to Equation 6. It is of course possible that a slow reduction of sodium triphenyl germanolate may have occurred. On the other hand, the reaction between the solvent and the metal may have been catalyzed by the presence of the germanium compounds. In the second experiment some sodium triphenyl germanide was evidently further reduced to disodium diphenyl germanide, as was indicated by the red color of the solution. In any case the reaction must have taken place initially according to Equation 6.

On passing dry air through the ammonia solution, on the completion of the initial reaction, the solution was decolorized and the amount of precipitate was increased. This was due to the oxidation of sodium triphenyl germanide to the corresponding germanolate, a reaction which is known to occur according to Kraus and Foster.

Summary

Ammonia reacts with triphenyl germanium bromide with the formation of ammonium bromide and triphenyl germanium amine. The amine

hydrolyzes with great ease in the presence of traces of moisture and loses ammonia readily, even at ordinary temperatures, with the formation of an imine and possibly some nitride.

Triphenyl germanium bromide is immediately and quantitatively ammonolyzed by potassium amide in liquid ammonia. In the presence of excess amide, the monopotassium salt, $(C_6H_5)_3GeNHK$, is formed. The amine is re-formed from the potassium salt on the addition of ammonium bromide.

Tritriphenyl germanium nitride was prepared by heating triphenyl germanium amine to 200° in *vacuo.* It crystallizes in the form of needles melting at 163–164°. It is soluble in petroleum ether and other common organic solvents and may be sublimed in *vacuo.*

Metallic sodium reacts with triphenyl germanium oxide in liquid ammonia with the formation of sodium triphenyl germanide and sodium triphenyl germanolate.

It is pointed out that the compounds of germanium are generally more reactive than are the analogous compounds of carbon.

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

THE REACTION BETWEEN ALKALI METAL ALKYLS AND QUATERNARY ARSONIUM COMPOUNDS

BY M. E. P. FRIEDRICH AND C. S. MARVEL

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In some of the early work on organic arsenic compounds Cahours[1] reported the preparation of pentamethylarsine by the action of zinc dimethyl on tetramethylarsonium iodide. The evidence for the existence of this penta-alkylarsine was slight and the work has never been confirmed. Previous attempts in this Laboratory to prepare the analogous penta-alkyl nitrogen[2] and phosphorus[3] compounds by the action of alkali metal alkyls on the corresponding -onium salts have not been successful. In view of Cahour's claim for the existence of pentamethylarsine, the work has been extended to the arsonium salts.

The methods used in the study of the reactions of alkali metal alkyls and arsonium salts were very similar to those used in the earlier work on nitrogen and phosphorus compounds. Lithium ethyl and lithium n-butyl were used in most of the experiments.

The first reaction studied was that between lithium n-butyl and tetraethylarsonium bromide. Low-boiling petroleum ether was used as a sol-

[1] Cahours, **Ann.,** 122, **337 (1862).**

[2] Hager with Marvel, THIS JOURNAL, **48,2689 (1926).**

[3] Coffman and Marvel, *ibid.,* 51, **3496 (1929).**

vent and the reaction mixture was carefully distilled out of contact with air or moisture in the hope of thus obtaining a high-boiling fraction that would prove to be the desired penta-alkyl arsenic compound. The only product that could be identified definitely was triethylarsine. Next an attempt was made to prepare a penta-alkyl arsenic compound from triethylarsine dibromide and lithium ethyl. Triethylarsine was the only product that was identified.

Since there seemed to be very little chance of isolating a pure stable penta-alkyl arsenic compound, it was decided to study some reactions that might lead to isomeric products of the type R_4AsR' and $R_3R'AsR$, as had been done before in the nitrogen series, and to determine whether or not their decomposition products would give any indication of the existence of penta-alkyl arsines in which the five valence bonds were equivalent. For this purpose the reactions between lithium n-butyl and tetra-ethylarsonium bromide and lithium ethyl and triethyl-n-butylarsonium bromide were investigated. The reaction products were worked up in such a manner as to make it possible to analyze the gaseous products. The reactions which occurred are shown by the following equations.

$$2LiC_4H_9 + 2(C_2H_5)_4AsBr \longrightarrow 2LiBr + 2(C_2H_5)_3As + C_2H_4 + C_2H_6 + C_4H_{10} + C_4H_2 \quad (1)$$

$$LiC_2H_5 + (C_2H_5)_3C_4H_9AsBr \longrightarrow LiBr + (C_2H_5)_2C_4H_9As + C_2H_4 + C_2H_6 \quad (2)$$

The fact that these two reactions give entirely different products shows that the arsenic atom did not at any stage of the reaction share five pairs of electrons with five hydrocarbon groups to give a penta-alkyl arsenic compound in which the alkyl groups were equivalent.

In working up these reaction mixtures it was found that the easiest way to identify the arsine was to allow it to undergo oxidation with air or oxygen. Instead of yielding the arsine oxides, it was found that triethylarsine gave diethylarsinic acid and diethyl-n-butylarsine gave ethyl-n-butylarsinic acid. These facts were checked by the use of the known arsines.

In analyzing the gaseous products of these reactions it was found that they were usually made up of less than 5% of unsaturated hydrocarbons and more than 95% of saturated hydrocarbons. This was the cause of considerable concern until it was found that ethylene was rather rapidly polymerized by a solution of a lithium alkyl to give non-gaseous products. Since the reaction mixtures containing in every case an excess of the lithium alkyl always stood for some two weeks under pressure it is not surprising that most of the olefins were polymerized before the tubes were opened.

One experiment was performed in which tetramethylarsonium iodide was treated with sodium triphenylmethyl in an attempt to isolate a compound analogous to the tetramethyltriphenylmethylammonium of Schlenk and Holtz.[4] There was some indication that a colored salt-like compound

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[4] Schlenk and Holtz, *Ber.*, 49,603 (1916).

was produced. However, the only product fully identified was triphenylmethane. The odor of trimethylarsine was apparent. No definite conclusion can be drawn from this experiment.

Experimental Part

Triethylarsine.—In a 5-liter two-necked flask fitted with a reflux condenser, a mechanical stirrer and a 1-liter separatory funnel were placed 168 g. of magnesium turnings and 3.8 liters of dry ether. The Grignard reagent was prepared by adding 720 g. of ethyl bromide in the usual manner. The air was swept out of the flask with a current of dry nitrogen and to the Grignard solution thus prepared was then added a solution of 300 g. of arsenic trichloride in 600 cc. of dry ether. During the addition of this solution stirring was maintained and the solution was kept at a temperature of about 20°. Stirring was then discontinued and the mixture was boiled under the reflux for about twenty-four hours. The reaction mixture was decomposed with ice water acidified with hydrochloric acid. The ether layer was separated and the water layer was extracted three times with more ether. The combined ether layers were dried over calcium chloride and distilled. After the ether was removed at ordinary pressures, the residue was distilled under reduced pressure in a current of dry nitrogen or carbon dioxide. The triethylarsine boiled at 65–70° at 25–30-mm. pressure. The yield was 150–173 g. (54–62% of the theoretical amount). Steinkopf and Müller[5] obtained yields of 40% of the theoretical amount of triethylarsine without refluxing the mixture.

Tetra-ethylarsonium Bromide.—A solution of 15 g. of triethylarsine and 21 cc. of ethyl bromide in 20 cc. of dry ether was heated at 98° in a sealed tube for about eight hours. The tube was cooled and opened. The salt was dissolved in absolute alcohol, then precipitated with dry ether and filtered with suction. The yield was 18 g. (75% of the theoretical amount). The product melted at 298–300° (uncorr.).

Anal. Subs., 0.5518: 19.62 cc. of 0.1043 N $AgNO_3$. Calcd. for $C_8H_{20}AsBr$: Br, 29.51. Found: Br, 29.45.

Triethyl-n-butylarsonium Bromide.—A solution of 15 g. of triethylarsine and 18 g. of n-butyl bromide in 20 cc. of dry ether was heated at about 98° in a sealed tube for about two days. The salt was purified by dissolving in absolute alcohol and precipitating with dry ether. The yield was 19 g. (75% of the theoretical amount). The product melted at 227° (uncorr.).

Anal. Subs., 0.1213: 4.59 cc. of 0.0893 N $AgNO_3$. Calcd. for $C_{10}H_{24}AsBr$: Br, 26.74. Found: Br, 26.99.

Diethyl-*n*-butylarsine.—To the Grignard reagent prepared from 24 g. of magnesium and 110 g. of ethyl bromide in 200 cc. of dry ether was added a solution of 60 g. of n-butyldichloro-arsine in 70 cc. of dry ether. The mixture was stirred and boiled under a reflux condenser for about eighteen hours. The reaction mixture was decomposed with ice water acidified with hydrochloric acid. The ether layer was separated, dried over calcium chloride and distilled. After the ether was removed, the residue was distilled under reduced pressure. The arsine boiled at 78° at 28 mm. The yield was 25 g. (44% of the theoretical amount); sp. gr. d_{20}^{20} 1.0306; n_D^{20} 1.4745.

The compound was not analyzed but a 5-cc. sample was heated in a sealed tube overnight with 5 cc. of ethyl bromide in 10 cc. of dry ether. The product was identical with the triethyl-n-butylarsonium bromide obtained from triethylarsine and n-butyl bromide.

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[5] Steinkopf and Müller, *Ber.*, 54B, 844 (1921).

Tetramethylarsonium Iodide.—A solution of methylmagnesium chloride was prepared by passing dry methyl chloride into a well-stirred suspension of magnesium turnings in dry ether. The strength of this solution was determined by titrating a portion with acid according to the method of Gilman, Wilkinson, Fishel and Meyers.[6] To 2 liters of this ether solution containing 3.02 moles of methylmagnesium chloride was added 165 g. of arsenic trichloride. Considerable solid separated and stirring was impossible. After standing overnight the mixture was decomposed with ice water acidified with hydrochloric acid. The mixture was distilled directly until the ether was removed and the distillate containing ether and trimethylarsine was dried over calcium chloride. To this solution an excess of methyl iodide was added. After several weeks the precipitated tetramethylarsonium iodide was filtered off and recrystallized from ethyl alcohol. The product seemed to sublime at 320–328°.

Anal. Subs., 0.2413: 9.78 cc. of 0.0893 *N* $AgNO_3$. Calcd. for $C_4H_{12}AsI$: I, 48.49. Found: I, 48.55.

Diethylarsinic Acid.—A sample of triethylarsine was allowed to stand in a loosely stoppered test-tube. The crust which formed on the surface was broken from time to time and the material gradually solidified. This solid product was recrystallized from ethyl acetate several times and it then melted sharply at 136–137°.[7] Some reddish oil was formed during the oxidation. This was entirely removed in the crystallization. The acid was titrated with standard alkali. Subs., 0.1275: 6.4 cc. of 0.1199 N NaOH. Neutral equivalent, calcd. for $C_4H_{10}AsO_2H$: 165.9. Found: 165.1. The same material was obtained by bubbling dry oxygen through a solution of triethylarsine in dry ether.

Ethyl-*n*-butylarsinic Acid.—This was first prepared by oxidizing diethyl-*n*-butylarsine with air in oxygen exactly as described above. The product was recrystallized from a mixture of benzene and finally melted at 93–96°.

To prove the structure of this product a sample was prepared by the general method for the synthesis of arsinic acids devised by Quick and Adams.[8]

To a well-stirred mixture of 20 g. of ethyl bromide and 70 cc. of 10 N sodium hydroxide was slowly added 34 g. of n-butyl dichloro-arsine. The mixture was stirred for a few hours, then filtered and evaporated to dryness. The residue was extracted with hot benzene and the arsinic acid was precipitated with petroleum ether. After several recrystallizations from a mixture of benzene and petroleum ether this product melted at 93–96°. A mixed melting point with the product obtained from the oxidation of diethyl-n-butylarsine showed that the two were identical. The product was titrated. Subs., 0.1229: 5.3 cc. of 0.1199 N NaOH. Calcd. for $C_6H_{14}AsO_2H$, neutral equivalent, 193.9. Found: 193.3.

General Procedure Followed in Studying the Reactions of the Lithium Alkyls and Quaternary Arsonium Salts

Lithium ethyl and lithium n-butyl were prepared and used in both petroleum ether (b. p. 40–45°) and a high-boiling paraffin oil in the manner previously described by Hager with Marvel.[2] The petroleum ether solutions were analyzed but no analysis was made on the solutions in the high-boiling oil. The arsonium salts were dried in a vacuum desiccator over sulfuric acid before use. When petroleum ether was used as a solvent for the reaction, the lithium alkyl was prepared exactly as described before and the reaction with the arsonium salt was carried out in a flask such as is shown in Fig. 1. The

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[6] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, 45, 150 (1923).

[7] Wigren, *Ann.*, 437, 288 (1924), gives the melting point as 133–134°.

Quick and Adams, THIS JOURNAL, 44, 811 (1922).

dried salt was introduced into the small bulb (A), which was then sealed. The glass apparatus containing the lithium alkyl solution was sealed on at B and the apparatus was connected to a mercury vapor pump, all of the air exhausted and the apparatus was sealed. The valve on the reaction vessel containing the lithium alkyl was broken and the solution was allowed to flow into the large Bulb D. The reaction flask was then sealed at B. Some glass beads were placed in the large reaction flask so that shaking the flask prevented caking of the reaction mixture. The salt was introduced into the solution of the lithium alkyl by tilting the apparatus. Gas evolution was noted in all of the experiments. The reaction mixtures were allowed to stand for about two weeks with occasional shaking. After this time the flask was opened at C and the gas collected in an evacuated bulb of the type shown in Fig. 3.

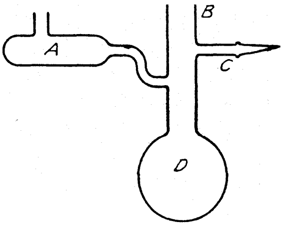

Fig. 1.

When the high-boiling paraffin oil was used as a solvent it was found more convenient to use the reaction vessel shown in Fig. 2. The dry salt was introduced in Bulb A (200 cc.). The solvent, mercury alkyl and lithium were placed in Bulb B (100 cc.). The system was evacuated with a mercury-vapor pump and sealed at C and D. E was a Gooch filter plate sealed into the apparatus. When the conversion of the mercury alkyl to the lithium alkyl was complete, as indicated by the settling of the lithium amalgam to the bottom of the solution, the oil solution was filtered over into the bulb containing the salt. These reaction mixtures were also allowed to stand for about two weeks and the gas was collected by opening at F.

The gas was collected by attaching the evacuated gas pipet (Fig. 3) to the side-arm of the reaction flask by means of heavy-walled pressure tubing. One stopcock of the gas pipet was opened and the tip on the reaction flask was broken inside the heavy tubing. The reaction flasks were heated to about 100° [illegible] of the gases when the high-boiling paraffin oil was used as a solvent. The gas in the pipet was brought to atmospheric pressure by introducing dry mercury until the pressure was equalized with atmospheric pressure.

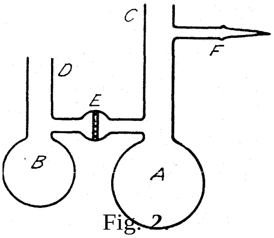

Fig. 2.

The first gas analyses were made by absorption and combustion methods. However, it was found much more satisfactory to determine the unsaturated hydrocarbons by absorption in bromine water and to determine the density of the remaining saturated hydrocarbons after drying with anhydrous magnesium perchlorate by means of an Edwards gas density balance.[9] A sample of each gas was burned to be sure that it was not air.

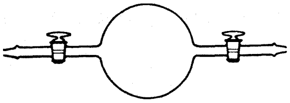

Fig. 3.

After removal of the gases in all of the later experiments, the flasks were opened. The odor of the arsine was always noticeable. From the high-boiling paraffin oil solutions it was impossible to isolate pure products of any sort. When petroleum ether was used as a solvent it was evaporated and the arsinic acids were obtained by allowing the residue to oxidize in the air.

Attempt to Prepare **Tetra-ethyl-n-butylarsenic.—After** a few preliminary trials the apparatus shown in Fig. 4 was used for this experiment. In Bulb A was placed 18 g. of carefully dried tetra-ethylarsonium bromide and some glass beads. The bulb was then

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[9] Directions for using this balance are given in Bureau of Standards Paper No. 89.

sealed. The reaction flask containing the lithium *n*-butyl solution was sealed on to the apparatus at C. The entire apparatus was evacuated with a mercury-vapor pump and carefully sealed. Then 0.048 mole of lithium n-butyl in 60 cc. of petroleum ether was introduced into Bulb B and the apparatus was sealed at C. The salt was slowly poured over into the lithium alkyl solution. Vigorous gas evolution was noted. The petroleum ether solution was poured back and forth from Bulb A in order that all of the salt would come into contact with the lithium n-butyl. After about two days the reaction mixture was filtered through the filter sealed into the apparatus at D into Flask E. The petroleum ether was then partially distilled back into B to wash the salt and again filtered. The gas was then removed from the apparatus by opening the side-arm on Flask B and the apparatus was evacuated to a pressure of 30 mm. The apparatus was then sealed at F. The solid left in Flask B was found to be lithium bromide and some unchanged tetra-ethylarsonium bromide.

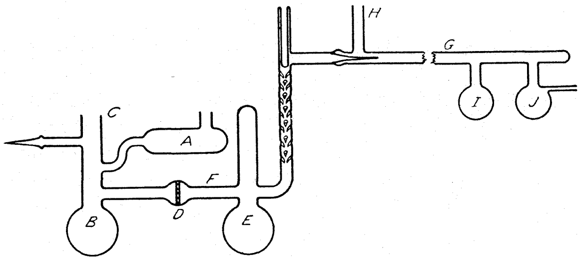


Fig. 4.

The petroleum ether solution in Flask E was then distilled. The two-bulb receiver was sealed onto the side-arm, evacuated and sealed. The valve at H was broken. The distillation flask was placed in an oil-bath and the receiver I was placed in an ice-bath. A first fraction was obtained up to about 54°. The bulb I was sealed off and a second fraction boiling up to 77° was collected in Bulb J. This bulb was sealed and about a half gram of liquid which boiled at 100–110° was collected in the tip of G. This was obtained by directly heating the bulb with a flame and the high-boiling temperature was undoubtedly due in part to superheating.

The first fraction was redistilled under atmospheric pressure and boiled at 40–65°. It did not have the characteristic arsine odor. The second fraction on redistillation in the air boiled at 65 to 140°. Most of the material came over at 139–140°, which indicated that it was nearly pure triethylarsine. A sample on standing in the air was oxidized to diethylarsinic acid. Another sample gave triethylarsine dibromide when treated with bromine. The small amount of high-boiling liquid was again distilled under atmospheric pressure and distilled below 150". It gave all of the tests for triethylarsine.

Lithium Ethyl and Tetraethylarsonium Bromide.—A solution of 0.095 mole of lithium ethyl in petroleum ether (b. p. 40–45°) was added to 25 g. (0.092 mole) of tetraethylarsonium bromide. A vigorous evolution of gas was noted but no color was produced. After two weeks the flask was cooled in an ice-bath, opened and the gas collected. It contained 1.4% of ethylene as shown by absorption in bromine water. The remaining gas was analyzed by combustion.

Anal. 60 cc. gas: 90 cc. of O_2. Vol. after combustion, 99.2 cc. Contraction, 50.8 cc. Vol. after absorption of CO_2 in alkali, 55.5 cc. CO_2, 43.7 cc. 48.7 cc. gas 89.9 cc. of O_2. Vol. after combustion, 94.5 cc. Contraction, 44.1 cc. Vol. after absorption of CO_2 in alkali, 58.3 cc. CO_2, 36.2 cc. (The gases were measured at the same temperatures and pressures.) Calcd. for ethane: contraction, CO_2: 1.25. Pound: 1.17, 1.22.

After the gas was collected, the reaction flask was opened, the reaction mixture filtered and the petroleum ether allowed to evaporate in the air. Diethylarsinic acid crystallized and after recrystallization melted at 136–137°.

For more accurate analysis of the gas the reaction was run in high-boiling paraffin oil. The reagents used were 2 g. of lithium, 20 g. of diethyl mercury and 23 g. of tetraethylarsonium bromide. The gas collected was analyzed by determining the density as mentioned in the general discussion.

Anal. (Gas density) bar. pressure, 742.00 mm.; gage readings with air, 705.9 mm.; 98.9 mm. Pressure, 607.0 mm. Total pressure, 135 mm. Gage readings with gas, 705.9 mm.; 98.9 mm. Pressure, 607.0 mm. Total pressure, 135 mm. Calcd. for C_2H_6: sp. gr., 1.049. Calcd. for C_2H_4; sp. gr., 0.978. Found: sp. gr., 1.00. (Absorption) 88.2 cc. of gas, 4.7 cc. lost by absorption in bromine water: 5.3% of unsaturated hydrocarbons.

The odor of the arsine was apparent in the paraffin oil solution but no arsinic acid was isolated.

Lithium n-Butyl and Tetraethylarsonium Bromide.—A solution of 0.04 mole of lithium n-butyl in petroleum ether was added to 11.11 g. (0.041 mole) of tetraethylarsonium bromide. A vigorous reaction occurred and gas evolution was noted. No attempt was made to collect this gas. The reaction flask was opened and the contents were filtered. On allowing the solution to stand in the air the petroleum ether evaporated and the arsine was oxidized to diethylarsinic acid, m. p. 136°.

A second reaction was carried out in high-boiling paraffin oil solution. The reagents used were 2 g. of lithium, 25 g. of di-n-butyl mercury and 23 g. of tetraethylarsonium bromide. After two weeks the reaction flask was opened and the gas collected.

Anal. (Gas density) bar. pressure, 742.3 mm.; gage readings with air, 713.5 mm.; 90.0 mm.; pressure, 623.5 mm.; total pressure, 118.8 mm. Gage readings with gas, 735.0 mm.; 66.1 mm.; pressure, 668.9 mm.; total pressure, 73.4 mm.; sp. gr. of gas, 1.62. (Absorption) 99.5 cc. of gas: 1.0 cc. lost by absorption in bromine water. 1.0% of unsaturated hydrocarbons. The density figures indicate that the gas is approximately 45% ethane and 55% butane. Such a mixture would have a specific gravity of 1.60.

Lithium Ethyl and Triethyl-*n*-butylarsonium Bromide.—A solution of 0.058 mole of lithium ethyl in petroleum ether was added to 175 g. (0.058 mole) of triethyl-*n*-butylarsonium bromide. After three weeks the mixture was cooled in ice, the reaction flask was opened and the gas collected. The gas density reported was determined after removal of the unsaturated hydrocarbons. Gas density: bar. pressure, 746.0 mm.; gage readings with air, 721.9 mm., 80.0 mm.; pressure, 641.9 mm.; total pressure, 104.1. Gage reading with gas: 725.8 mm., 76.1 mm.; pressure, 649.7 mm.; total pressure, 96.3: sp. gr., 1.08.

The specific gravity of this gas indicated that it was nearly pure ethane. It undoubtedly was contaminated with some petroleum ether vapors. After removal of the gas the reaction mixture was worked up as described before and ethyl-n-butylarsinic acid melting at 92" was obtained.

This reaction was run in paraffin oil using 2 g. of lithium, 20 g. of diethyl mercury and 25 g. of triethyl-n-butylarsonium bromide. The gas was collected and analyzed.

Anal. (Gas density) bar. pressure, 744 mm.; gage readings with air, 707.2 mm., 96.1 mm.; pressure, 611.1 mm.; total pressure, 132.9 mm.; gage reading with gas, 711.3 mm., 92.0 mm.; pressure, 619.3 mm.; total pressure, 124.7 mm.: sp. gr., 1.065. (Absorption) 96.5 cc. of gas: 2.4 cc. lost by absorption in bromine water: 2.5% of unsaturated hydrocarbons. These results indicated that the gas was nearly pure ethane with some ethylene and possibly a small amount of butane.

Lithium n-Butyl and Triethyl-n-butylarsonium Bromide.—A solution of 0.048 mole of lithium n-butyl in petroleum ether was added to 5 g. of triethyl-n-butylarsonium bromide. From the reaction mixture ethyl-n-butylarsinic acid, m. p. 87–89°, was isolated.

The reaction was repeated in paraffin oil using 2 g. of lithium, 25 g. of di-*n*-butyl mercury and 25 g. of triethyl-n-butylarsonium bromide. The gas was collected and analyzed. The unsaturated gases were removed after the density was taken on the original gas.

Anal. (absorption) 91.7 cc. of gas: 5.2 cc. lost by absorption in bromine water: 5.6% of unsaturated hydrocarbons. Gas density: bar. pressure, 743.4 mm.; gage readings with air, 715.0 mm., 88.5 mm.; pressure, 626.5 mm.; total pressure, 116.9 mm.; gage readings with gas, 735.0 mm., 66.0 mm.; pressure, 669.0 mm.; total pressure, 74.4 mm.; sp. gr., 1.57. This specific gravity indicated a mixture of about 47% of ethane and 53% of butane.

Lithium-n-Butyl and Triethylarsine Dibromide.—A solution of 0.047 mole of lithium n-butyl in petroleum ether was added to 7.8 g. (0.024 mole) of triethylarsine dibromide. A vigorous reaction occurred and gas was evolved. This gas was collected and by a gas density determination the specific gravity was found to be 1.801. Since petroleum ether vapors were present, this value was not very significant. However, not much ethane could have been present. The odor of an arsine was apparent when the flask was opened but not enough arsinic acid was isolated for positive identification.

Lithium Ethyl and Triethylarsine Dibromide.—A solution of 0.06 mole of lithium ethyl in petroleum ether was added to 9.5 g. of triethylarsine dibromide. No attempt was made to collect the gas. From the petroleum ether solution diethylarsinic acid, m. p. 136–137°, was isolated in the usual way.

Sodium Triphenylmethyl and Tetramethylarsonium Iodide.—A solution of 0.012 mole of sodium triphenylmethyl in dry ether was added with shaking to 5 g. of tetramethylarsonium iodide. The color of the solution faded and a solid of dull brick-red color remained in the flask. This solid was washed with anhydrous ether a few times. The red solid was not affected by dry carbon dioxide. When an attempt was made to recrystallize the solid from pyridine it appeared to decompose. The pyridine solution turned pale green. Triphenylmethane was isolated from the pyridine solution. If a compound related to the penta-alkyl ammonium of Schlenk and Holtz[4] had formed, it should have reacted with dry carbon dioxide to give tetramethylarsonium triphenylacetate.

Effect of Heat on Solutions of Lithium Alkyls in High-Boiling Paraffin Oil.—A solution of lithium ethyl in high-boiling paraffin oil did not give off gas when heated to 100°. Above this temperature gas was evolved. When such a solution was heated to 250° the gas obtained was about 75% unsaturated hydrocarbons. Gas density measurements indicated about 3% of hydrogen and 22% of ethane as the remaining constituents of the gas.

Lithium n-butyl in high-boiling paraffin oil solution did not liberate much gas until heated to about 173°. Gas evolution then became very marked. The gas collected was 94% unsaturated hydrocarbons. Gas density measurements indicated that the original gas was about 94% butylene, 3% butane and 3% hydrogen.

Effect of Lithium Alkyl Solutions on Ethylene.—A solution of lithium n-butyl was prepared from 1 g. of lithium and 10 g. of di-*n*-butyl mercury in 100 cc. of high-boiling paraffin oil. Ethylene from a tank of the commercial product was admitted under pressure. The pressure soon dropped and then more ethylene was introduced. In about two weeks 620 cc. of ethylene had been introduced. When an attempt was made to recover the ethylene, only 120 cc. of gas could be recovered on heating the solution to 100°. This gas was not pure ethylene but contained some inert material, probably air, which must have been present in the commercial gas. The ethylene did not remain in the oil as such because a similar experiment without the lithium alkyl showed that all of the gas could be recovered.

A similar experiment was tried with lithium ethyl instead of lithium n-butyl. The results were essentially the same. Only a small amount of gaseous hydrocarbons could be recovered by heating the paraffin oil solution.

Another experiment was made using *a* solution of 0.031 mole of lithium n-butyl in 50 *cc.* of petroleum ether (40–45°). Ethylene was absorbed readily and within two weeks a white solid began to appear on the surface of the solution. This solid has not been studied further.

The authors desire to express their thanks to Dr. G. F. Smith for help in some of the analytical problems met in this work.

Summary

1. Lithium alkyls have been found to react readily with tetra-alkyl arsonium bromides to give trialkylarsines and hydrocarbons which come from disproportionation of the alkyl groups. No evidence of the formation of a stable penta-alkyl arsenic compound was obtained.

2. Lithium alkyls have been found to cause polymerization of ethylene to give non-gaseous products.

3. It has been observed that trialkylarsines are oxidized by air to give dialkylarsinic acids.

4. Improved methods for the preparation of some trialkylarsines and tetra-alkyl arsonium salts have been reported.

URBANA, ILLINOIS

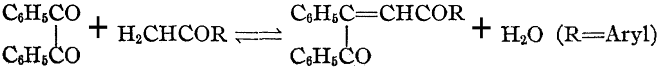
[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

DIACYLSTYRENES. II

BY CHARLES F. H. ALLEN AND J. ROCKWELL HUBBARD

RECEIVED AUGUST 12, 1929 PUBLISHED JANUARY 8, 1930

In an earlier paper[1] it was shown that benzil easily condensed with acetophenones that did not have a substituent in the position ortho to the carbonyl group.



$$\begin{array}{l}C_6H_5CO\\ \quad|\\ C_6H_5CO\end{array} + H_2CHCOR \rightleftharpoons \begin{array}{l}C_6H_5C{=}CHCOR\\ \quad|\\ C_6H_5CO\end{array} + H_2O \quad (R{=}\text{Aryl})$$

We have extended this investigation to include methyl ketones having different types of rings and found that diacylstyrenes are always formed under the conditions previously described. Methyl a-thienyl (I) and methyl a-furyl (II) ketones were selected as examples of heterocyclic compounds.

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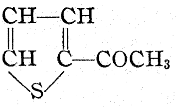
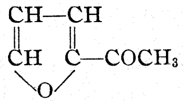
[1] Allen and Rosener, THIS JOURNAL, 49, 2110 (1927).


I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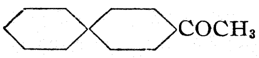
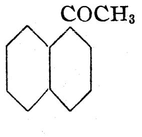
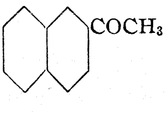
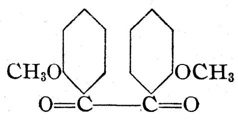

III

Since the acetophenones used in the earlier paper had only alkyl substituents, the p-phenyl compound (III) was taken, to show that an aryl group would not prevent the reaction.


IV


V


VI

We then examined the naphthyl methyl ketones for two reasons: (1) x-ray data indicate that one ring is bent over on the other, so that it might possibly exert a hindrance because of spatial relations; (2) in methyl a-naphthyl ketone (IV) there is an ortho substituent, that is, the second ring is fused on in an ortho position. It was found that while methyl P-naphthyl ketone (V) readily formed a diacylstyrene, the a-compound did not react. Thus rings in the ortho position offer the same kind of hindrance as other groups in the ortho position; elsewhere they have no effect.

The following acetophenones, which have become available since our earlier paper, were also investigated—p-ethyl, 3,4-dichloro, 3-nitro[2] and 2,4-dihydroxy. The first two formed diacylstyrenes, as expected. The last one, having an ortho substituent, did not react. With the third compound, the nitro group was attacked by alkali, and a mixture of high melting substances formed which it was not thought worth while to identify. Japp and Maitland[3] have previously examined pinacolone and found that it formed trimethacetylstyrene.

Finally, to see whether the effect of o-substituents was confined to the methyl ketone, *o,o'*-dimethoxybenzil (VI) in place of benzil was employed with acetophenone. As it was recovered quantitatively, unchanged, it may be concluded that groups in the ortho position of either component prevent the reaction from taking place. Since the effect is independent of the nature of the group, it is evidently due to spacial relations of some sort.

Experimental

Preparation **of β-Naphthyl** Methyl Ketone.—To the Grignard reagent prepared from 7 g. of magnesium and 40 g. of methyl iodide in 150 cc. of dry ether was added with stirring a warm solution of 14.5 g. of β-naphthonitrile in 50 cc. of the same solvent;

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[2] For this substance we are indebted to Dr. B. B. Corson.

[3] Japp and Maitland, J. *Chem. Soc.*, 85, 1502 (1904).

the small amount of solid nitrile adhering to the dropping funnel was rinsed in with **30** cc. more ether. There was very little apparent action. After standing overnight, most of the ether was distilled by gradually immersing the flask in boiling water. The viscous residue was decomposed by ice and sulfuric acid in the usual way, the oily layer taken up in ether, dried and fractionally vacuum distilled; **6.5 g.** of a yellow oil that readily crystallized was separated. There was considerable gummy residue. We were unable to isolate any of this ketone by the Friedel–Crafts reaction from naphthalene and either acetyl chloride or acetic anhydride. The other ketones were prepared by methods already in the literature.

The condensation with benzil was carried out exactly the same as in the earlier paper, except that ethyl acetate was used as a solvent for recrystallization. The results are summarized in the table.

DERIVATIVES OF α,β-DIBENZOYLSTYRENE

No.	Ketone used	M. p., °C.	Formula	Analyses Calcd., % C	 H	 Found, % C	 H
I	Methyl a-thienyl[m]	152	$C_{20}H_{14}O_2S$	75.5	4.4	75.3	4.5
II	Methyl α-furyl[b]	168	$C_{20}H_{14}O_3$	79.5	4.6	79.7	4.6
V	Methyl β-naphthyl	152	$C_{26}H_{18}O_2$	86.2	4.9	86.2	5.0
III	p-Phenylacetophenone[c]	132	$C_{28}H_{20}O_2$	86.6	5.2	85.8	5.2
VII	p-Ethylacetophenone[e]	117	$C_{24}H_{20}O_2$	84.7	5.9	84.4	6.0
VIII	3,4-Dichloroacetophenone[d,e]	199	$C_{22}H_{14}O_2Cl_2$	69.2	3.7	69.1	3.9

[a] Prepared by excellent directions of Stadnikov and Goldfarb, *Ber.*, **61**, 2341 (1928). [b] Sandelin, *ibid.*, **33**, 493 (1900). [c] Adams and Noller's method, THIS JOURNAL, **46**, 1889 (1924). [d] Roberts and Turner, *J. Chem. Soc.*, **130**, 1855 (1927). [e] Recrystallized from anisole, insoluble in ethyl acetate and carbon tetrachloride.

o,o'-**Dimethoxybenzil**[2] (VI) **and** Acetophenone.—A methyl alcoholic solution of these two substances was treated in the same manner; as there was no apparent reaction after five minutes the whole was refluxed for eight hours. The dimethoxybenzil was recovered quantitatively.

We were unable to isolate any crystalline material from the reddish gums produced when either methyl @-pyridyketone or p-amino-acetophenone was used.

This work has been assisted by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Summary

1. The investigation of the condensation of benzil with derivatives of acetophenone has been extended to include those in which the substituent group is a ring. It has been found that the reaction takes place readily unless the position ortho to the carbonyl group is a part of the ring.
2. Methyl ketones having heterocyclic ring systems can be used equally well in place of acetophenone.
3. The same kind of hindrance is observed whether the o-substituent is in the benzil or the ketone.

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[CONTRIBUTION NO. 55 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

CATALYSIS IN ORGANIC CHEMISTRY. I. REACTIONS OF ETHERS WITH ACID CHLORIDES, ACIDS AND ANHYDRIDES[1]

BY H. W. UNDERWOOD, JR., AND R. L. WAKEMAN

RECEIVED AUGUST 15, 1929 PUBLISHED JANUARY 8, 1930

Ethers are usually described as inert compounds; the carbon-oxygen bond is firmly held, and drastic treatments, such as heating with hydriodic acid or anhydrous aluminum chloride, are generally employed to split ethers. Descudé[2] and Wedekind and Haeussermann[2] noted that esters and alkyl chlorides are formed by the reactions of ethyl and methyl *iso*-amyl ethers with acetyl chloride and with benzoyl chloride in the presence of anhydrous zinc or ferric chloride. More information about transformations of this type would be desirable on account of the frequent use of ethers as (presumably inert) solvents or diluents, and also as a contribution to our knowledge of factors which increase the reactivity of ethers. This paper deals with an investigation of the reactions of ethyl ether with a series of representative acid chlorides; experiments with *iso*propyl, *n*-butyl and iso-amyl ethers are also described. It was found that diphenyl ether and anisole behave like aromatic hydrocarbons in their reactions with acetyl and benzoyl chlorides, and yield ketones through the introduction of an acetyl or benzoyl group into the ring.

We have shown that a number of acids and anhydrides can be converted into esters by treatment with ethyl ether in the presence of hydrogen bromide.[3]

Discussion of Experiments and Interpretation of Results

All of the temperatures given are uncorrected.

Purification of Ethers.—The ethyl ether employed in our experiments was purified by Norris' procedure.[4] Pure isopropyl, n-butyl and *iso*-amyl ethers were dried for several days with anhydrous sodium sulfate and distilled before use.

Reactions of Ethers with Acid Chlorides

Preliminary Experiments and General Procedure.—In preliminary experiments the action of anhydrous aluminum, ferric and zinc chlorides in promoting the reactions

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[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 R. L. Wakeman in partial fulfilment of the requirements for the degree of Master of Science.

[2] Descudé, *Compt. rend.*, 132, 1129 (1901); *Ann. chim. phys.*, [7] *29*, 497 (1903); Wedekind and Haeussermann, *Ber.*, 34, 2081 (1901).

[3] Fenton and Gostling [*J. Chem. Soc.*, *73*, 554 (1898)] stated that ethyl esters of dihydroxymaleic, oxalic, acetic, benzoic, boric and stearic acids are obtained by allowing the acids to stand for several days with anhydrous ethyl ether containing dry hydrogen bromide.

[4] Norris, "Experimental Organic Chemistry," McGraw-Hill Book Co., New York City, 1924, p. 73.

of ethyl ether with acetyl and benzoyl chlorides was investigated. Esters were obtained in each trial; since anhydrous zinc chloride gave the best yields and was most easily handled it was employed in all subsequent work.

The ether was added to a mixture of the acid chloride and finely powdered, anhydrous zinc chloride in a small, dry flask. A reflux water condenser, with a calcium chloride tube in the top, was attached immediately, and the mixture was heated at its boiling point until the reaction appeared to be complete; usually two to three hours of heating was required. The reaction mixture was then cooled in ice and shaken several times with two or three volumes of cold water until practically free from zinc chloride; in some cases a little pure ethyl ether was added to dilute the mixture. The ether layer was next dried with anhydrous sodium sulfate. After most of the ether had been removed by distillation, the residue was fractionated in case the expected reaction product was a liquid, or allowed to stand until crystallization occurred if the ester was a solid. Liquid esters were collected over a range of 5 to 6°; if necessary, solid esters were washed with cold, dilute sodium carbonate solution and crystallized from suitable solvents. A 10 to 15% excess of ether and approximately 0.25 mole of zinc chloride per mole of acid chloride were employed.

Ethyl Ether.—The acid chlorides investigated and the percentage yields of ethyl esters obtained are as follows: acetyl, 40; chloro-acetyl, 35; propionyl, 15; *n*-butyryl, 21; *iso*valeryl, 20; benzoyl, 60; phenylacetyl, 79; oxalyl, 4; diphenic acid chloride, 77. The amounts of the acid chlorides used were 31.4, 15, 20, 20, 16, 56, 9.7, 12.2 and 2.2 g., respectively.

No esters were obtained from benzenesulfonyl chloride (20 g.) or *p*-toluenesulfonyl chloride (15 g.). In order to determine whether compounds containing labile chlorine atoms would behave like acid chlorides, 50 g. of benzyl chloride and 15 g. each of *o*-nitrochlorobenzene, 2,4-dinitrochlorobenzene and picryl chloride were heated with ethyl ether in the presence of zinc chloride. Each halogen compound was recovered unchanged; benzyl chloride gave some high-boiling tar.

A mixture of 25.4 g. of *o*-phthalyl chloride, 10.3 g. of ethyl ether and 4.2 g. of anhydrous zinc chloride was refluxed for about two hours; white crystals were formed suddenly. After the contents of the flask had been cooled to room temperature, the solid was collected on a filter, washed with water and dried. The crystals, which weighed 15.5 g., were identified as phthalic anhydride. The liquid portion of the reaction mixture was washed twice with an equal volume of water, dried with anhydrous sodium sulfate and fractionated. Two grams of diethyl phthalate was isolated. The results of this experiment indicate that diethyl phthalate may be transformed into phthalic anhydride by zinc chloride; small scale experiments with some known diethyl phthalate proved that this splitting takes place.

Ethyl Ether and 3,5-Dinitrobenzoyl Chloride.—We prepared ethyl 3,5-dinitrobenzoate by treatment of a small quantity of the dinitrobenzoyl chloride with an excess of pure, dry ethyl ether in the presence of anhydrous zinc chloride. An investigation is now being carried out to determine whether this type of reaction can be employed in the identification of aliphatic (and possibly aromatic) ethers; the results will be discussed in a later paper. Mulliken[5] has described the use of 3,5-dinitrobenzoyl chloride for the identification of alcohols.

Higher Aliphatic Ethers.—The reactions of acetyl chloride with isopropyl (5 g.), *n*-butyl (20 g.) and iso-amyl (15 g.) ethers gave 30, 68 and 48% yields of the corresponding acetates. Benzoyl chloride was converted into isopropyl, *n*-butyl and *iso*-amyl benzoates; the yields were 10, 45 and 40%. Twenty-eight and 57% yields of

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[5] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York City, 1904, Vol. I, pp. 168–172.

n-butyl propionate and n-butyl n-butyrate were obtained by heating propionyl chloride (16 g.) and n-butyryl chloride (23 g.) with n-butyl ether.

Isolation of Alkyl Chlorides.--Small amounts of ethyl, *iso*propyl, n-butyl and *iso*-amyl chlorides were obtained from some of our reaction mixtures. More information about these alkyl chlorides is given in a later paper.[6]

Aromatic Ethers.--The behavior of the following pairs of compounds in the presence of anhydrous zinc chloride was studied: diphenyl ether and acetyl chloride, anisole and acetyl chloride, diphenyl ether and benzoyl chloride, anisole and benzoyl chloride. Each mixture was allowed to stand for half an hour at room temperature, and then heated under reflux in a water-bath for two hours. Hydrogen chloride was evolved and a dark viscous mass was formed in each case. The mixtures were cooled and diluted with several volumes of cold water and some ethyl ether. After being washed with water until practically free from zinc chloride, the ether solutions of the reaction products were dried with anhydrous sodium sulfate; then the solvent was removed by distillation. The products thus isolated were viscous oils which partly solidified upon long standing; in some cases it was necessary to fractionate the oils. The solids were pressed on a porous tile and crystallized from alcohol and water or from pure ethyl ether. The melting points as well as other physical properties and resistance to hydrolysis of our products indicate that they are 4-phenoxyacetophenone, *p*-acetylanisole, 4-phenoxybenzophenone and p-benzoylanisole; Kipper, and Gattermann, Ehrhardt and Maisch[7] prepared these compounds from diphenyl ether and anisole by treatment of the ethers with acetyl and benzoyl chlorides in the presence of anhydrous aluminum chloride. From two 17-g. lots of diphenyl ether we obtained 9 g. of 4-phenoxybenzophenone and 7 g. of 4-phenoxyacetophenone; two 10.8-g. lots of anisole gave 6 g. of p-benzoylanisole and 0.5 g. of *p*-acetylanisole. There was no evidence of the formation of esters in the reactions. One-gram samples of each (uncrystallized) reaction product were heated under reflux for an hour with 10 cc. of 10% sodium hydroxide solution; by extraction with pure ethyl ether practically all of the initial material was recovered in each case. Evidently the carbon-oxygen bonds in diphenyl ether and anisole are not readily broken by zinc chloride; the ketones which we obtained were previously prepared with better yields by the use of anhydrous aluminum chloride in place of zinc chloride. Consequently, no more aromatic ethers were investigated.

Reactions of Ethyl Ether with Acids and with Anhydrides

Preliminary Experiments and General Procedure.—The acids and most of the anhydrides employed in our experiments were pure Eastman products; succinic and diphenic anhydrides were synthesized. It was found that treatment of glacial acetic acid with a slight excess of pure, dry ethyl ether in the presence of anhydrous zinc chloride did not give a good yield of ethyl acetate.

Hydrogen bromide was prepared by dropping bromine on moist red phosphorus; moisture and bromine were removed by passing the gas through a drying train containing red phosphorus, calcium chloride and phosphorus pentoxide. The dry hydrogen bromide was passed into pure, anhydrous ethyl ether in a flask attached to a reflux water condenser, with a calcium chloride tube in the top, for about seven hours; the mixture was cooled from time to time but not continuously. This procedure did not completely saturate the ether, but it gave a fairly concentrated solution. It was found that treatment with hydrogen bromide for a longer time and continuous cooling were necessary for the complete saturation of the ether.

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[6] Underwood and Toone, THIS JOURNAL, **52,** 391 (1930).

[7] Kipper, *Ber.,* **38,** 2490 (1905); Gattermann, *ibid.,* *22,* 1129 (1889); Gattermann, Ehrhardt and Maisch, *ibid.,* **23,** 1199 (1890).

About 75 cc. of the ether–hydrogen bromide mixture was added to each of the acids and anhydrides in an Erlenmeyer flask. The latter was closed by a tight-fitting stopper held in place by wire and covered with collodion. The reaction mixtures were allowed to stand for ten to twelve days. Each flask was then attached to a reflux water condenser provided with a calcium chloride tube, and the contents were boiled for three hours. After being cooled to room temperature, each reaction mixture was shaken two or three times with an equal volume of cold 10% sodium hydroxide solution until very slightly alkaline; then it was washed with an equal volume of cold water and dried with anhydrous sodium sulfate. Finally the excess ether was removed by distillation and the residue was fractionated if the expected ester was a liquid, or allowed to stand until crystallization occurred if the ester was a solid; if necessary, solid esters were washed with cold, dilute sodium carbonate solution and crystallized from suitable solvents.

Yields of Esters.—The acids investigated and the percentage yields of ethyl esters obtained are as follows: acetic, 8; chloro-acetic, 30; propionic, 34; n-butyric, 41; isovaleric, 42; oxalic, 8; malonic, 6; succinic, 16; benzoic, 28; phenylacetic, 56; hydrocinnamic, 80; p-toluic, 23; mandelic, 24; anisic, 5; p-chlorobenzoic, 10; o-nitrobenzoic, 5; m-nitrobenzoic, 42; p-nitrobenzoic, 10; 3,5-dinitrobenzoic, 27; *p*-aminobenzoic, 1; o-phthalic, 9; diphenic, 16. Three grams of hydrocinnamic acid, 4 g. of *p*-toluic acid and 10 g. each of the other acids were used. No esters were obtained from stearic, picric, *p*-toluenesulfonic and 2,4,6-trinitrobenzoic acids; Victor Meyer's esterification rule would lead one to expect that the trinitrobenzoic acid would not esterify.

The anhydrides investigated and the percentage yields of ethyl esters obtained are as follows: acetic, 13; propionic, 23; n-butyric, 38; isovaleric, 41; succinic, 13; benzoic, 49; o-phthalic, 13; diphenic, 25. Ten grams of each anhydride was used.

An investigation of the mechanism of the reactions of ethyl ether with acids and anhydrides in the presence of dry hydrogen bromide[6] has shown that the amount of the latter present influences the yields of esters. If two moles of hydrogen bromide per mole of ethyl ether is used, all of the ether is converted into ethyl bromide. In the experiments described above the same ether–hydrogen bromide mixture was used for each compound in a series and the results are comparable. Check runs with acetyl chloride, benzoyl chloride and acetic anhydride and different lots of ether–hydrogen bromide mixtures gave yields of esters which were nearly the same as those previously obtained.

Summary

In the presence of anhydrous zinc chloride, pure ethyl ether reacts with the chlorides of acetic, chloro-acetic, propionic, n-butyric, *iso*valeric, benzoic, phenylacetic, diphenic, o-phthalic, oxalic and 3,5-dinitrobenzoic acids to form ethyl esters. o-Phthalyl chloride gives phthalic anhydride as well as diethyl phthalate. Under the conditions tried, benzenesulfonyl and p-toluenesulfonyl chlorides do not form esters, and the chlorine atoms in benzyl chloride, o-nitrochlorobenzene, 2,4-dinitrochlorobenzene and picryl chloride are not replaced by ethoxy groups. Isopropyl, *n*-butyl and *iso*-amyl acetates and benzoates are obtained by the treatment of acetyl and benzoyl chlorides with isopropyl, n-butyl and *iso*-amyl ethers. Diphenyl ether and anisole behave like aromatic hydrocarbons when heated with acetyl and benzoyl chlorides in the presence of anhydrous zinc

chloride; ketones are formed by the introduction of an acetyl or benzoyl group into the aromatic nucleus.

Acetic, chloro-acetic, propionic, n-butyric, isovaleric, oxalic, malonic, succinic, benzoic, phenylacetic, hydrocinnamic, *p*-toluic, mandelic, anisic, p-chlorobenzoic, *o*-, *m*- and p-nitrobenzoic, 3,5-dinitrobenzoic, *p*-aminobenzoic, o-phthalic and diphenic acids and the anhydrides of acetic, propionic, n-butyric, isovaleric, succinic, benzoic, o-phthalic and diphenic acids are converted into ethyl esters by treatment with anhydrous ethyl ether containing dry hydrogen bromide. Stearic, picric, *p*-toluenesulfonic and 2,4,-6-trinitrobenzoic acids do not react with ethyl ether in the presence of hydrogen bromide.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION NO. 56 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY. MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

CATALYSIS IN ORGANIC CHEMISTRY. II. MECHANISM OF THE REACTIONS OF ETHERS WITH ACID CHLORIDES, ACIDS AND ANHYDRIDES

BY H. W. UNDERWOOD, JR., AND G. C. TOONE

RECEIVED AUGUST 15, 1929 PUBLISHED JANUARY 8, 1930

In a previous paper[1] it was pointed out that a number of acid chlorides, acids and anhydrides are converted into esters by treatment with aliphatic ethers in the presence of anhydrous zinc chloride or hydrogen bromide. Zinc chloride might increase the reactivity of aliphatic ethers by loosening the alkyl groups so that a metathesis of the type $RCOCl + R'OR' = RCOOR' + R'Cl$ would occur. The possibility that aliphatic ethers may be split into two or more compounds capable of independent existence also deserves consideration. Experiments described in this paper show that ethyl, *iso*propyl, n-butyl and *iso*-amyl ethers yield small amounts of the corresponding alcohols and unsaturated hydrocarbons when heated with anhydrous zinc chloride. When an alcohol thus formed is esterified by an acid chloride, splitting of the ether continues, and the hydrogen chloride produced may convert some of the alcohol into an alkyl chloride. Equations for the transformations of acetyl chloride and ethyl ether might be written as follows

$$CH_3CH_2OCH_2CH_3 = CH_3CH_2OH + CH_2{=}CH_2$$
$$CH_3CH_2OH + CH_3COCl = CH_3COOCH_2CH_3 + HCl$$
$$CH_3CH_2OH + HCl = CH_3CH_2Cl + H_2O$$

The reaction of ethyl ether with acetyl chloride takes place in the presence of a very small amount of anhydrous zinc chloride, and the latter can be used several times; apparently zinc chloride acts as a true catalyst.

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[1] Underwood and Wakeman, THIS JOURNAL, 52, 387 (1930).

We have also shown that ethyl, isopropyl, n-butyl and iso-amyl ethers are converted into alkyl bromides and alcohols when treated with dry hydrogen bromide.

Discussion of Experiments and Interpretation of Results

All the temperatures given are uncorrected.

Purification of Ethers.—Ethyl ether was purified by the method cited in a previous paper.' An explosion occurred during the distillation of isopropyl ether which had been purchased as pure; tests showed that this ether contained peroxides. The procedure described below was employed for the purification of isopropyl, n-butyl and iso-amyl ethers. In order to remove peroxides each compound was washed with one-fifth its volume of 10% potassium iodide solution as often as necessary (one to ten times); the iodine produced in this treatment was removed by shaking the ether with one-fifth its volume of 10% sodium thiosulfate solution. Next the compound was washed with one-fifth its volume of water, then cooled in ice, shaken with one-fourth its volume of a mixture of sulfuric acid and water (equal volumes of each) and finally washed with water. After being dried with anhydrous sodium sulfate the ether was distilled. The boiling points of the purified ethers were as follows: ethyl, 34–34.5°; isopropyl, 68–68.5°; n-butyl, 139.5–140.5°; iso-amyl, 169–170°.

Ethers **and** Anhydrous Zinc Chloride.—Ethyl, isopropyl, n-butyl and iso-amyl ethers were refluxed for two hours with anhydrous zinc chloride; one half mole of the latter per mole of ether was used. In each experiment the top of the reflux water condenser was connected with two flasks; one of these contained 10 g. of bromine to absorb unsaturated hydrocarbons, and the other flask was a trap. The quantities of ethers used are as follows: ethyl, 44.4 g.; isopropyl, 12.3 g.; n-butyl, 26 g.; *iso*-amyl, 31.6 g. n-Butyl ether yielded 0.5 cc. of a liquid boiling at 70–130°; a drop of this distillate gave the odor of n-butyl acetate when mixed with a drop of acetyl chloride. The remainder of the liquid boiling at 70–130° was added to 0.1 g. of 3,5-dinitrobenzoyl chloride; the mixture was allowed to stand for five minutes, placed in hot water for two minutes and filtered. The solid left on the filter was added to 5 cc. of 3 N sodium carbonate solution and well stirred in order to remove excess dinitrobenzoyl chloride. The insoluble residue was filtered and washed with 5 cc. of 3 N sodium carbonate solution and 5 cc. of water. After three crystallizations from alcohol the solid melted at 63–64"; this is the melting point of n-butyl 3,5-dinitrobenzoate.[2] A parallel experiment with some n-butyl ether which had not been treated with zinc chloride gave no ester. Iso-amyl ether yielded 0.6 cc. of a liquid boiling at 70–165°. By use of the procedure described above, 0.1 *g.* of iso-amyl 3,5-dinitrobenzoate (m. p. 60–61") was isolated. **A** parallel experiment with iso-amyl ether which had not been heated with zinc chloride gave no ester.

The bromine used to absorb unsaturated hydrocarbons which might be formed in the splitting of the ethers was treated with 10% sodium thiosulfate solution to remove unchanged bromine and the resulting mixture was extracted with 40 cc. of pure ethyl ether. The ether layer was dried with anhydrous sodium sulfate and distilled. No dibromides were isolated in any of our preliminary experiments; probably the amounts of unsaturated hydrocarbons formed were too small to be detected by this method. However, it was found that the ethers apparently contained traces of unsaturated compounds after heating with zinc chloride, since small portions of the ethers decolorized very dilute potassium permanganate solution.

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[2] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York City, 1904, Vol. I, p. 168.

In preliminary experiments with ethyl and isopropyl ethers we were unable to prepare dinitrobenzoates from the distillates. However, four drops of the distillate from isopropyl ether gave the iodoform reaction. Three and one-half moles of each ether was refluxed for three hours with zinc chloride and distilled. No portions of the distillates boiled as high as the corresponding alcohols, but dinitrobenzoates were obtained from the first 8 cc. of each distillate; these fractions also gave the iodoform test, and enough of the latter for a melting point was secured. Parallel experiments with ethers which had not been heated with zinc chloride gave negative results.

It was necessary to use 500 g. of the ethers in order to isolate the dibromides of the unsaturated hydrocarbons formed in the splittings by zinc chloride; very small amounts of these dibromides were obtained.

Anisole, phenetole and diphenyl ether (0.1 mole of each) were heated under reflux for two hours with anhydrous zinc chloride (0.05 mole). Upon distillation of each mixture the ether was recovered practically quantitatively; all of the liquid boiled within one degree. The distillates gave no color test for phenol when treated with ferric chloride solution; a violet color was readily obtained by adding one drop of dilute phenol solution and one of ferric chloride solution to a portion of each distillate. Evidently the carbon–oxygen bonds in these aromatic ethers are not broken by anhydrous zinc chloride under the conditions tried.

Ethers and Acid Chlorides.—The experiments described below were carried out to secure information about the products other than esters which are formed in the reactions of aliphatic ethers with acid chlorides. In each run 0.4 mole of zinc chloride per mole of acid chloride was used. Fifty-two and three-tenths grams of acetyl chloride and 54.2 g. of ethyl ether gave 37.8 and 30.2% yields of ethyl acetate and ethyl chloride and a trace of ethylene dibromide; 20.4 g. of isopropyl ether and 19.6 g. of acetyl chloride gave 66.5 and 30.6% yields of isopropyl acetate and isopropyl chloride and 1.8 g. of propylene dibromide. By distillation of the reaction mixture from 50 g. of n-butyl ether and 27.5 g. of acetyl chloride we obtained 65.7 and 29.9% yields of n-butyl acetate and n-butyl chloride and 10.6% of butylene dibromide. One-tenth mole of acetyl chloride and 0.11 mole of iso-amyl ether gave 12 and 6% yields of *iso*-amyl acetate and iso-amyl chloride, and 0.1 g. of isopropylethylene dibromide.

Catalytic Action of Anhydrous Zinc Chloride.—A mixture of 31.4 g. of acetyl chloride and 32.6 g. of pure anhydrous ethyl ether was heated under reflux for three hours with 5.44 g. of anhydrous zinc chloride, and then distilled from the latter through a long fractionating column. The yield of ethyl acetate was 77%. (This result shows that some ethyl acetate is lost in the isolation procedure, involving extractions with ether and washing the ether solution, described in a preceding paper[1] and followed in previous experiments.) The zinc chloride was used for three more runs; the yields of ethyl acetate were 78, 77 and 79%. Evidently zinc chloride acts as a true catalyst in this reaction.

Ethers and Hydrogen Bromide.—Hydrogen bromide was prepared and dried by the procedure described in a previous paper.[1] In experiments with n-butyl ether (22.1 g.), *n*-butyl ether (22.1 g.) + glacial acetic acid (10.2 g.), and n-butyl ether (22.1 g.) + acetic anhydride (17.3 g.) hydrogen bromide was passed into the liquids for six hours, with cooling during the last two hours; 0.36 mole of hydrogen bromide was absorbed in each case. Dry hydrogen bromide was passed into 20.4 g. of glacial acetic acid until 0.143 mole had been absorbed; this required two hours. The flasks containing these mixtures were closed with tight-fitting stoppers held in place by wire and covered with collodion. After standing for ten days at room temperature, the liquids were refluxed for three and one-half hours in a water-bath, and the layers which had formed were separated. In each case the non-aqueous layer was washed with dilute sodium carbonate solution and with water, dried with anhydrous sodium sulfate and distilled through a long fractionating column. The n-butyl ether yielded 29.2 g. of n-butyl bromide. The n-butyl etheracetic acid mixture gave 20.4 g. of n-butyl bromide, 1 g. of n-butyl acetate and 9.5 g. of acetic acid. From the acetic anhydride–ether mixture we obtained 16.3 g. of n-butyl bromide, 2 g. of n-butyl acetate and 8 g. of impure acetic acid. After standing for ten days, mixtures of 20.4 g. of acetic acid + 0.143 mole of hydrogen bromide, and 17.3 g. of acetic anhydride + 0.2 mole of hydrogen bromide were distilled through a long fractionating column; the former gave 17 g. of acetic acid and the latter yielded 2 g. of acetyl bromide and 9 g. of acetic acid. These experiments show that acetic anhydride is converted into acetyl bromide and acetic acid by reaction with hydrogen bromide.

In order to determine the behavior of n-butyl ether when treated with less hydrogen bromide than was used in previous experiments, hydrogen bromide was passed into 19.7 g. of the ether (0.15 mole) until 0.25 mole had been absorbed. After the mixture had stood for sixteen hours, it was heated under reflux for three hours. The two layers which formed were separated, washed with dilute sodium carbonate solution, dried with anhydrous sodium sulfate and distilled through a long fractionating column. Nineteen grams of n-butyl bromide and 1.5 g. of n-butyl alcohol were obtained; the latter was identified by preparation of the 3,5-dinitrobenzoate. Similar experiments with ethyl, isopropyl and iso-amyl ethers gave the alkyl bromide and a small amount of the corresponding alcohol in each case. By use of an excess of hydrogen bromide ethyl ether was entirely converted into ethyl bromide.

Summary

When heated with anhydrous zinc chloride ethyl, isopropyl, n-butyl and iso-amyl ethers yield small amounts of the corresponding alcohols and unsaturated hydrocarbons. When an alcohol thus formed is esterified by an acid chloride, splitting of the ether continues, and the hydrogen chloride produced in the esterification converts some of the alcohol into an alkyl chloride. Under the conditions tried the carbon-oxygen bonds in anisole, phenetole and diphenyl ether are not broken by zinc chloride. The reaction of ethyl ether with acetyl chloride takes place in the presence of a very small amount of anhydrous zinc chloride, and the latter can be used several times; apparently zinc chloride acts as a true catalyst.

Ethyl, isopropyl, n-butyl and iso-amyl ethers are converted into alcohols and alkyl bromides by treatment with dry hydrogen bromide. The reaction of acetic anhydride with anhydrous hydrogen bromide gives acetyl bromide and acetic acid.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION NO. 57 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

CATALYSIS IN ORGANIC CHEMISTRY. III. DECOMPOSITIONS OF ESTERS BY ANHYDROUS ZINC CHLORIDE

BY H. W. UNDERWOOD, JR., AND O. L. BARIL

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During the course of investigations of the reactions of ethers with acid chlorides[1] it was noted that aliphatic ethers yield alcohols and unsaturated hydrocarbons when heated with anhydrous zinc chloride and that diethyl phthalate is converted into phthalic anhydride. These transformations involve the splitting of the bond between the oxygen atom and alkyl groups in the ethers and in the ester. In this paper we present evidence which shows that a number of esters undergo decompositions of this or similar types in the presence of anhydrous zinc chloride.

Discussion of Experiments and Interpretation of Results

All the temperatures given are uncorrected.

General Procedure.—Pure, freshly distilled esters were used in our experiments; 0.5 mole of anhydrous zinc chloride per mole of ester was employed. Unsaturated hydrocarbons formed by the decomposition of the esters were collected as dibromides by the procedure described in a previous paper.[1] Unless otherwise stated, each reaction mixture was distilled from the zinc chloride after refluxing; the distillate was then fractionated. In some experiments the residue in the reaction flask after distillation was dark colored and somewhat tarry; however, all the distillates were free from tar, and were easily separated into the components.

Ethyl Formate, Ethyl Acetate, Ethyl Propionate and Ethyl *n*-Butyrate.—No evidence of decomposition was found in experiments with these compounds. One-half mole of ethyl formate and acetate, one-third mole of the butyrate and one-fifth mole of ethyl propionate were used; in each case more than 95% of the ester was recovered; all the mixtures were heated under reflux for three hours before distillation.

Methyl and Ethyl Benzoates, Diethyl Phthalate.—From 30 *g*. of ethyl benzoate which had been refluxed with anhydrous zinc chloride for two hours we obtained 7.5 g. of benzoic acid,[2] 3 g. of benzene,[2] 2 g. of ethylene dibromide and carbon dioxide. Evidently zinc chloride converts some of the benzoic acid formed by the decomposition of the ester into benzene and carbon dioxide. We obtained benzene by heating some known benzoic acid with zinc chloride.

Thirty-four grams of methyl benzoate yielded 5 g of benzoic acid,[2] 4 g. of benzene[2] and 9 g. of the unchanged ester. No evidence of the formation of an unsaturated hydrocarbon was found. Three lots (34 g. each) of methyl benzoate were heated with zinc chloride for three hours, and the vapors from the top of the condenser were passed into 10 g. of bromine; treatment of the latter in the usual way[1] gave no ethylene dibromide. In these experiments a dark tarry residue was found in the reaction flask; possibly this was formed from the fragments of the methyl groups by the zinc chloride.

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[1] Underwood and Wakeman, THIS JOURNAL, 52, 387 (1930); Underwood and Toone, *ibid.*, 52,391 (1930).

[2] The tests described by Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York City, 1904, Vol. I, were used for the identification of this compound.

A mixture of 44.4 g. of diethyl o-phthalate and 13.6 g. of anhydrous zinc chloride solidified after being heated for half an hour under reflux. Distillation of the product gave 22 g. of phthalic anhydride;[2] 2.5 g. of ethylene dibromide was also isolated.

Ethyl and Methyl Salicylates.—One-fourth mole of ethyl salicylate and one-fifth mole of the methyl ester were refluxed with anhydrous zinc chloride for one hour and one and one-half hours, respectively. The reaction mixtures were cooled and extracted several times with pure ethyl ether; the solutions thus formed were shaken with water to remove zinc chloride, dried with anhydrous sodium sulfate and fractionated. From the ethyl salicylate we obtained 4 g. of phenol,[2] 4 g. of *o*-ethylphenol,[3] 3.5 g. of the unchanged ester, I g. of ethylene dibromide and carbon dioxide. Apparently two types of decomposition occurred—one involved the removal of ethylene and the other the elimination of carbon dioxide from the ester group. Methyl salicylate gave 6 g. of *o*-cresol,[2] 7 g. of the unchanged ester and carbon dioxide.

Iso-amyl Acetate, Iso-amyl *n*-Butyrate, Iso-arnyl Benzoate.—A mixture containing 32.5 g. of iso-amyl acetate was refluxed for three hours and distilled. Twenty-seven grams of the ester was recovered and 1.4 g. of acetic acid[2] was isolated. The recovered iso-amyl acetate decolorized a small amount of dilute potassium permanganate solution and apparently contained a trace of an unsaturated compound. Decomposition of iso-amyl acetate takes place only to a slight extent.

After three hours' refluxing, 31.6 g. of iso-amyl n-butyrate yielded 6 g. of n-butyric acid,[2] 8 g. of unchanged ester, 7 g. of a liquid with the properties of the dimer of isopropylethylene, 0.2 g. of isopropylethylene dibromide and 4 g. of a high-boiling residue (possibly a high polymer of isopropylethylene). These products were difficult to fractionate. Evidently anhydrous zinc chloride splits iso-amyl n-butyrate into n-butyric acid and isopropylethylene, and polymerizes some of the latter.

From 38.4 g. of iso-amyl benzoate which had been heated under reflux with anhydrous zinc chloride for three hours, we obtained 11 g. of benzoic acid,[2] 0.9 g. of benzene,[2] 0.5 g. of a liquid with the properties of the dimer of isopropylethylene, 0.8 g. of isopropylethylene dibromide and carbon dioxide.

Ethyl Cinnamate.—Thirty-five and two-tenths grams of ethyl cinnamate was refluxed with anhydrous zinc chloride for three-fourths of an hour. The products are 3 g. of styrene, 6.5 g. of distyrene,[4] carbon dioxide and 5 g. of a dark brown material which had the properties of metastyrene. We also obtained 0.9 g. of ethylene dibromide. Apparently zinc chloride brings about the removal of ethylene and carbon dioxide from ethyl cinnamate, and polymerizes some of the styrene which is formed.

Diethyl Oxalate and Succinate.—When heated with anhydrous zinc chloride for an hour, one-fourth mole of diethyl oxalate was transformed into a white solid which weighed 33.5 g. This material was insoluble in hot and cold water and did not melt at 360". In order to determine whether the solid contained oxalic acid, a sample was heated for some time at 150°; no sublimation occurred. Ignition of the product caused the distillation of an organic liquid and gave a white residue which contained zinc. Another experiment with diethyl oxalate was carried out and the gases evolved during the heating were investigated. Carbon dioxide, ethyl chloride and a gas which behaved like a saturated aliphatic hydrocarbon were found; no ethylene was detected. The results of the experiments indicate that zinc chloride reacts with diethyl oxalate to give ethyl chloride and a zinc salt; some of the ester is split into carbon dioxide

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[3] This compound was identified by the preparation of the tribromo derivative; the procedure described by Stoermer and Kahlert, Ber., 35, 1631 (1902), was used.

[4] The styrene and distyrene were identified by the preparation of the dibromides; the procedures described by Glaser, Ann., 154, 154 (1870), and by Fittig and Erdmann, *ibid.*, 216, 190 (1882), were used.

and a saturated aliphatic hydrocarbon, possibly butane. Diethyl succinate behaved like diethyl oxalate when heated with anhydrous zinc chloride.

Diethyl Malonate.—From one-fourth mole of diethyl malonate which had been refluxed with anhydrous zinc chloride for three hours we obtained 6 g. of ethyl acetate, 6 g. of unchanged ester and carbon dioxide; 0.2 g. of ethylene dibromide was secured. In a check run we isolated 8 cc. of a liquid which had the boiling point and other properties of n-pentane. Evidently two types of decomposition occurred—one involved the removal of both ethylene and carbon dioxide from one of the ester groups and the other involved the elimination of carbon dioxide from each ester group.

Summary

When ethyl formate, acetate, propionate and *n*-butyrate are heated with anhydrous zinc chloride each ester remains unchanged. Under similar conditions diethyl o-phthalate gives phthalic anhydride and ethylene, and ethyl benzoate yields benzoic acid, benzene and ethylene. Ethyl salicylate is transformed into phenol and o-ethylphenol through the loss of ethylene and carbon dioxide. From methyl benzoate we obtained benzoic acid and benzene, and from methyl salicylate we secured o-cresol and carbon dioxide. Anhydrous zinc chloride splits iso-amyl acetate, n-butyrate and benzoate into the corresponding acids and isopropylethylene, and polymerizes some of the latter. Ethyl cinnamate yields styrene, distyrene, metastyrene, carbon dioxide and ethylene. Diethyl malonate gives ethyl acetate, n-pentane, ethylene and carbon dioxide. Anhydrous zinc chloride reacts with diethyl oxalate forming ethyl chloride and a zinc salt; some of the ester is decomposed into carbon dioxide and a saturated aliphatic hydrocarbon. Diethyl succinate behaves like diethyl oxalate.

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[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

SKRAUP'S REACTION APPLIED TO THE PHENYLENEDIAMINES. PREPARATION OF THE PHENANTHROLINES AND RELATED DIPYRIDYLS

BY C. R. SMITH

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The Skraup reaction as applied to monoamines has proved to be a valuable synthetic method, but the double Skraup reaction, either in the original or in a modified form, applied to diamines, has generally given unsatisfactory results, especially with *p*- or m-phenylenediamine. It seems that either no attempts have been made to apply the reaction to o-phenylenediamine or, more probably, that no pure compounds were isolated from the resulting products and hence the results were not reported.

The writer has studied the production of phenanthrolines from the phenylenediamines and has found that results which compare favorably with the average monoamine as to yield and ease of purification can be obtained with the m- and *p*-diamine. o-Phenylenediamine, however, did not give o-phenanthroline but a compound, $C_{12}H_8N_2O$, crystallizing in deep, yellow colored needles. This compound was oxidized to a carboxylic acid which, on heating, loses carbon dioxide, forming a colorless base not identical with α,α-dipyridyl. o-Phenanthroline could not be separated from the Skraup reaction products, although it might have escaped detection, because of the large amount of amorphous products formed and the lack of information in regard to the properties of *o*-phenanthroline, which had not then been prepared.

According to Richter's "Organic Chemistry,"[1] o-phenanthroline is obtained from o-aminoquinoline, but no reference or description is given. a-Methyl-o-phenanthroline, however, has been prepared from 1-amidoquinaldine.

A. Kaufmann and Radoslav Radosevic[2] concluded that *p*-phenanthroline can be obtained only in small yield from *p*-phenylenediamine. They preferred to employ the corresponding aminoquinoline prepared from *p*-nitroaniline.

As the result of a study of the Skraup reaction, as applied to m- and *p*-phenylenediamines, with arsenic acid as the oxidizing agent, the conclusion has been reached that the important factors are water concentration and the method and time of heating. It is important to start the digestion with a high water concentration and to permit the gradual escape of water vapor as the reaction proceeds. There is a limited range of water concentration that is optimum; at a greater concentration the proper reaction will not take place at all and at a lower concentration the reaction is too vigorous for good results. This regulation of concentration is conveniently effected by using short air condensers; water condensers are used only toward the end of the reaction when the danger of tar formation is greatest.

A violent reaction is not permissible as with aniline and some other amines. The *m*- and *p*-diamines differ in behavior to such an extent that a method applicable to one is not suitable for the other. For example, in the case of *m*-phenylenediamine the reaction starts at a low water concentration and the temperature can be slowly elevated. Such treatment is not suitable for the $-diamine reaction. o-Phenylenediamine is a highly reactive substance, sensitive to oxidizing agents and subject to ring closure between the amino groups. Highly colored tarry products were always obtained from this compound, which yielded only a small amount of the yellow crystalline compound previously mentioned.

In following the directions of Skraup and Vortmann[3] in the preparation

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[1] Vol. III, p. 207, English translation of 11th German edition.

[2] A. Kaufmann and Radoslav Radosevic, *Ber.*, 42, 2612 (1909).

[3] Skraup and Vortman. *Monatsh.*, 3, 571 (1882).

of *m*-phenanthroline and the corresponding dicarboxylic acid and dipyridyl the writer obtained results similar to those of Blau.[4] The methods given below improve the yields and ease of manipulation of this phenanthroline as well as the *p*-phenanthroline and the corresponding derivatives.

The only sources of the α,β- and β,β-dipyridyls have been the corresponding phenanthrolines. If the o-phenylenediamine could be made to produce o-phenanthroline in good yield, it might prove to be a convenient method of preparing α,α-dipyridyl. The negative results so far obtained from the o-diamine and the poor yield obtained from the *o*-aminoquinoline do not offer much promise. The writer has prepared α,α-dipyridyl conveniently from the sodium and pyridine reaction.[5] It can also be formed in less than 15% yield by heating copper picolinate[6] or by heating pyridine in sealed tubes under pressure with ferric chloride.[7]

It has usually been assumed that acrolein is produced in the Skraup reaction and that this first condenses with the amino group and is then oxidized with ring closure. No instance has been recorded in which an intermediate product of acrolein with the amine has been isolated which can be further changed to the end-product.

Mann[8] attempted to prepare quinoline from the acrolein–aniline condensation product, with a negative result. The author, using the *m*-phenylenediamine condensation product, did not succeed in obtaining any phenanthroline. While the experiments with acrolein were conducted in an attempt to improve yields, they are of interest in considering the mechanism of the Skraup reaction.

The *p*-phenylenediamine gave better yields by the recommended procedure than the m-diamine, which is commonly regarded as the easier to manipulate. By the addition of alkali previous to oxidation with permanganate, the yield of dicarboxylic acid from either phenanthroline is more than doubled. A nearly quantitative yield of β,β-dipyridyl results when the dicarboxylic acid is heated in glycerine suspension. This method does not work well with α,β-dicarboxylic acid. In this case the elimination of one carboxyl group is effected by heating in an oil-bath at 200°, while the remaining one is removed by heating to a higher temperature. The yield of α,β-dipyridyl is nearly quantitative.

The writer prepared o-phenanthroline from o-aminoquinoline with some difficulty and found it to be similar to the isomeric phenanthrolines. This reaction might be considerably improved. The yellow compound $C_{12}H_8N_2O$ from o-phenylenediamine was obtained with such difficulty

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[4] Blau, *Monatsh.*, 13, 330 (1892).

[5] C. R. Smith, THIS JOURNAL, 46, 414 (1924).

[6] Blau, *Monatsh*, 10, 375 (1889).

[7] Hein and Retter, *Ber.*, 61, 1790 (1929).

[8] Mann, *J. Chem. Soc.*, 121, 2178 (1922).

and in such small yield that the carboxylic acid and the base produced on heating it were barely examined. A further study of these compounds would prove interesting.

Experimental

***p*-Phenanthroline.**—Fifty grams of *p*-phenylenediamine is mixed with 200 cc. of glycerine in a 2-liter Erlenmeyer flask. A mixture of 100 cc. of concentrated sulfuric acid and 100 cc. of arsenic acid (specific gravity of 1.80 and containing about 55% of As_2O_5) is slowly added whiie the mixture in the flask is agitated. Heat is applied carefully to produce and maintain a gentle ebullition, the flask being loosely covered with a small glass funnel to permit the escape of steam. After about one-half hour the contents should begin to turn brown. The funnel is then replaced by a short tube used as an air condenser. After heating is continued for about two hours, a test to determine the approximate amount of unaltered diamine is made by removing 1 cc. of the reaction mixture, diluting to 5 cc. with water and adding an excess of alcohol. *p*-Phenylenediamine sulfate separates on cooling if an appreciable quantity of the material is still unchanged, indicating that the heating should be continued with the air condenser until the test is essentially negative. The heating may now be continued under a water condenser for two hours, making the total time of digestion about five hours. The reaction mixture is now cooled and diluted with several portions of water, strong ammonia is added in excess, and the phenanthroline is extracted with several portions of benzol before the mixture has had time to cool. These extractions should be made as hot as is possible with the use of benzol by digesting solvent and mixture on the steam-bath preliminary to separation in the separatory funnel. The combined benzol extractions contain little tar, but nearly all of the phenanthroline with a little unaltered diamine. After evaporation of the benzol the residual p-phenanthroline is distilled without a thermometer, leaving the tar in the flask. The *p*-phennathroline while still liquid is poured in a thin steam into a large volume of water with continuous stirring and allowed to crystallize as the hydrate, which is filtered off and dried. To further purify and free it from unaltered diamine, it is liquefied with boiling water and poured again into a large volume of water. The product is then very satisfactory but can be further purified by being dissolved in alcohol or acetic acid and poured into water. The purification is not difficult when the Skraup reaction has been properly conducted. The yield is 65 g. of phenanthroline hydrate, representing about 60% of the theoretical.

β,β-Dipyridyl-dicarboxylic Acid.—The p-phenanthroline oxidizes best when it is finely divided and the reaction is conducted in alkaline solution. Twenty-five grams of p-phenanthroline hydrate is melted in about 500 cc. of hot water and poured into approximately 3 liters of cold water; 10 g. of potassium hydroxide is added and the cooled mixture is oxidized with 50 g. of potassium permanganate. The manganese dioxide is coagulated by heating to boiling and filtered off. The filtrate is evaporated to small volume, cooled and any phenanthroline which may separate is filtered off. The solution is now made just acid with acetic acid and digested on the steam-bath to remove the carbon dioxide present; the dicarboxylic acid is precipitated by the addition of copper acetate. The copper salt is decomposed by hydrogen sulfide from a suspension in boiling water. The dicarboxylic acid is obtained from the filtrate by evaporation and crystallization in the usual way.

β,β-Dipyridyl.—The decomposition of the dicarboxylic acid is best effected by heating it with sufficient glycerine to completely wet it. Gentle heating removes the carbon dioxide. The mixture is diluted with water, made alkaline with caustic soda and the dipyridyl extracted with ether. The dipyridyl distils over at 300 to 301" (corr.).

***m*-Phenanthroline.**—Fifty grams of m-phenylenediamine is mixed with 200 cc. of glycerine in a 2-liter flask. A mixture of 100 cc. of concentrated sulfuric acid and 100 cc. of arsenic acid (specific gravity of 1.80) is slowly added while the mixture is agitated in the flask. Heating is conducted as with *p*-phenylenediamine, but the loss of steam is permitted to take place more rapidly. A thermometer should be suspended in the mixture to insure that the temperature at ebullition is below 140" for about three hours of heating. The reaction has begun when a small test sample on dilution and the addition of ammonium hydroxide shows a flocculent precipitate. A short air condenser is employed during the 3-hour period. The temperature is permitted to rise gradually by alternating the air and water condensers until it reaches 150°, when a two-hour digestion with the water condenser completes the reaction. Caution should be increased at the last stage to avoid the formation of an excessive amount of tar.

The hot benzol extraction is made and the phenanthroline residue is distilled as with the *p*-diamine. The further purification is also conducted in the same way.

An extended series of experiments was conducted to study the effect of varying empirically the proportions of sulfuric acid, arsenic acid and glycerine, the same quantity (50 g.) of the diamine being used. While the results were not always uniform, because the conditions cannot be rigidly controlled, the proportions reported gave the best results. The best yield of benzol extract was 55 g., and the yield of pure dihydrate was 40 to 45 g.

The attempt to pass acrolein into the reacting mixture to facilitate and increase phenanthroline production resulted instead in loss. Acrolein was also passed into the diamine dissolved in glycerine until a heavy buff-colored precipitate was no longer produced. The sulfuric acid and arsenic acid were then added and the reaction was allowed to proceed as usual. Very little phenanthroline was formed.

A quantity of the condensation product of acrolein with the diamine was prepared by passing the gas into its solution in water. The product was amorphous and insoluble in acetone, alcohol and all other solvents tried. An experiment to subject this material to the Skraup reaction yielded no phenanthroline that could be separated.

Variations in the method of adding the reagents did not improve matters. In one experiment glycerine, *m*-diamine and arsenic acid were added slowly in one part to the sulfuric acid mixed with glycerine. An insoluble compound was formed which did not appear to be phenanthroline, but might possibly be the acrolein condensation product.

α,β-Dipyridyl-dicarboxylic Acid.—The yield of dicarboxylic acid is more than doubled by getting the phenanthroline in a finely divided condition and by the addition of alkali. The theoretical quantity of permanganate is used.

Melt twenty-five grams of dihydrate in 500 to 700 cc. of hot water and pour into 3 liters of cold water, agitating while the crystallization takes place to form it in a finely divided condition. Add ten grams of caustic potash, followed by 50 to 55 g. of potassium permanganate dissolved in water and added in small portions. Heat to boiling, filter off the manganese dioxide and evaporate the filtrate to low volume. Cool, filter off any separated unaltered phenanthroline, make acid with acetic acid and digest on the steam-bath. Instead of the silver salt, the writer uses advantageously the lead salt, which is formed by adding lead acetate and digesting until it becomes crystalline.

Suspend the lead compound in a large volume of hot water and pass in hydrogen sulfide. It is important to keep the mixture hot and pass in a large excess of gas to insure the complete precipitation of the lead. Add charcoal, Nter off lead sulfide and charcoal and evaporate to dryness on the steam-bath. Take up with water, filter off the crystals, evaporate the filtrate for further crystals and combine all fractions. The yield of dicarboxylic acid is about 80 to 85% of the theoretical.

α,β-Dipyridyl-monocarboxylic Acids.—When the dicarboxylic acid is heated in an oil-bath to 190–200°, two different monocarboxylic acids are formed. The principal acid, described at length by Skraup, crystallizes in long woolly needles, but the second isocarboxylic acid crystallizes in prismatic needles, a small amount subliming up the sides of the vessel. A quantity of this was collected and analyzed.

Anal. Calcd.: C, **66.00;** H, 4.00. Pound: **C, 65.78;** H, **4.21.**

The α,β-isomonocarboxylic acid melts at 152–154°. When the acid is heated to about 290°, carbon dioxide is evolved and α,β-dipyridyl is formed.

α,β-Dipyridyl.—It has been found that the yield of dipyridyl produced by directly heating the dicarboxylic acid, instead of using the calcium salt, is very good if each carboxyl group is removed at the lowest possible temperature. The dicarboxylic acid is placed in a small distilling bulb, which is immersed in an oil-bath. The bath is carefully heated to and maintained at **200'** until all evolution of gas from the first carboxyl has ceased. The flask is removed and heated in a sand-bath until evolution of the second carboxyl is complete. The flask can now be heated over a direct flame until the α,β-dipyridyl is distilled off, and only a small amount of tarry residue is left. It distils completely at 298°.

Skraup Reaction with *o*-Phenylenediamine.—When the o-diamine is treated similarly to the *p*-diamine, the addition of ammonia brings down a dark colored precipitate. This is dissolved in acid and precipitated with ammonia several times to free it from coloring matter. The precipitate is finally washed with acetone and dried. A large volume of boiling benzol is used to extract a deep yellow compound crystallizing in silky needles. Final purification is effected by recrystallizing from benzol after filtering the hot solution previously digested with charcoal. The pure crystals melt at **253°** (corr.).

Anal. Calcd. for $C_{12}H_8N_2O$: C, **73.50;** H, **4.08;** N, **14.3.** Pound: C, **73.70, 73.45;** H, **3.96, 4.00;** N (by Dumas), **15.0.**

The substance is scarcely soluble in any of the usual solvents. It is slightly soluble in hot benzol or hot alcohol.

It is possible that some o-phenanthroline is formed, but the methods of separation were not adequate to separate it. The results were always variable, and sometimes even none of the yellow compound could be isolated.

Oxidation of $C_{12}H_8N_2O$.—When the compound was oxidized by means of alkaline permanganate, a carboxylic acid crystallizing in needles and melting at **167'** was formed. When this acid was heated above the melting point, carbon dioxide was evolved and a residue formed which finally distilled undecomposed. When recrystallized from water this compound formed needles which melted at 113°. This substance was very soluble in hot water or cold dilute acids. On cooling the water solution, or neutralizing the acid solution with ammonia, the needles were again formed.

***o*-Phenanthroline.**—Ten grams of o-aminoquinoline was mixed with **25** cc. of glycerine, **12** cc. of sulfuric acid and **12** cc. of arsenic acid. The digestion was carried out similarly to that of *p*-phenylenediamine. After the reaction was considered ended, a large volume of water was added, followed by ammonia in slight excess. **A** black tarry precipitate was produced which was filtered off. A large excess of soda lye was added to the filtrate to precipitate the o-phenanthroline, which slowly crystallized in prismatic needles. The crystals were filtered off, washed with a little water, dissolved in acid and reprecipitated with soda lye. The precipitate was filtered, washed and dried. The dried product, weighing two grams, was extracted with boiling benzol, decolorized with charcoal, filtered and evaporated. The residue was crystallized from water after treatment with charcoal. Drying over sulfuric acid for several days resulted in **8.97%** loss of water; calcd. for $1H_2O$, **9.09.** The hydrate began to melt at **91°** and finished at 95°. The anhydrous phenanthroliie melted at 97°.

Anal. Calcd. for $C_{12}H_8N_2$: C, **80.00;** H, **4.40.** Found: C, **80.29;** H, **4.73.**

o-Phenanthroline distils undecomposed above 300°. It is soluble in alcohol, benzol and acetone, but insoluble in petroleum ether. It gives a red color with ferrous salts similar to the color obtained from α,α-dipyridyl. It was shown to be *o*-phenanthroline by oxidation with alkaline permanganate, forming a dicarboxylic acid crystallizing in needles. On heating, the dicarboxylic acid lost carbon dioxide and gave α,α-dipyridyl, as shown by its melting point (68°) and agreement with the known substance in odor, crystalline form and reaction with ferrous sulfate. The dicarboxylic acid was isolated by filtering off the manganese dioxide, making just acid with sulfuric acid, then alkaline with ammonia and evaporating to dryness. The residue was extracted with hot absolute alcohol. The acid left after evaporation of the alcohol crystallized from water in needles.

Summary

1. The double Skraup reaction can be satisfactorily applied to the *m*- and *p*-phenylenediamines with proper observance of water concentration, temperature and time of heating. The separation and purification of the respective phenanthrolines are described.

2. Oxidation of the phenanthrolines to their dicarboxylic acids by permanganate is best conducted at low temperatures with the addition of alkali.

3. β,β-Dipyridyl is satisfactorily prepared by heating its dicarboxylic acid in glycerine. α,β-Dipyridyl is prepared from its dicarboxylic acid by first eliminating one carboxyl at 200–210° and the other at 280–290°.

4. The double Skraup reaction when applied to o-phenylenediamine could not be made to yield *o*-phenanthroline but resulted only in a variable and small yield of a yellow crystalline substance, $C_{12}H_8N_2O$.

5. o-Phenanthroline was prepared from o-aminoquinoline. Its identity was established by oxidation to the dicarboxylic acid, which gave α,α-dipyridyl on heating.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH]

THE PREPARATION OF GAMMA-d-MANNONIC LACTONE

BY WILLIAM L. NELSON AND LEONARD H. CRETCHER

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Mannosaccharic lactone is a substance possessed of quite extraordinary properties.[1] The investigation of this lactone has been under way in this Laboratory for some time and has been especially time-consuming because of the difficulty of the preparation of the lactone in good yield. Fischer[2] reports only 2% on the basis of the weight of ivory nut meal hydrolyzed and oxidized and 7.5% from the oxidation of mannose.

The yield from the oxidation of pure mannonic lactone, however, is 30–35% according to Fischer[2] and even higher by the recently published method of Kiliani.[3]

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[1] Cf. Butler and Cretcher, THIS JOURNAL, **51**, 2167 (1929), for literature references.

[2] Fischer, *Ber.*, **24**, 539 (1891).

[3] Kiliani, *ibid.*, **54**, 456 (1921).

It would thus appear that a simple method for the preparation of the latter substance is desirable.

Mannonic lactone was obtained in poor yield by Pischer and Hirschberger[4] by oxidation of mannose with bromine. The product of the oxidation was a sirup which would not crystallize even after standing for months. He states that for the preparation of the crystalline lactone it is necessary to convert to the phenylhydrazide, from which the desired product can be obtained on hydrolysis with aqueous barium hydroxide. The use of phenylhydrazine renders this method too expensive and inconvenient.

By application of the method of oxidation of sugars by bromine in the presence of buffering salts recently described by Hudson and Isbell,[5] we have been able to prepare y-mannonic lactone from mannose in good yield. The lactone crystallizes on evaporation of the aqueous solution obtained after removal of excess bromine and hydrobromic acid. The method has also been successfully applied to the mannose-containing solution obtained on hydrolysis of ivory nut meal. It was not necessary to isolate the sugar before oxidation.

Experimental Part

Preparation from Mannose.—Eighteen grams of d-mannose was oxidized in the manner described by Hudson and Isbell[5] for the oxidation of glucose to gluconic acid. Their directions were followed in every particular except that after removal of hydrobromic acid, the solution was not boiled with calcium carbonate to convert the sugar acid to a salt, but was evaporated under reduced pressure to a thick sirup. Mannonic lactone usually crystallized during the process of evaporation; if not, crystallization took place immediately on scratching the walls of the flask. Fifteen cc. of absolute alcohol was added to facilitate removal from the flask. After filtering and air drying the product weighed 15.5 g. and melted at 148–151°. On recrystallization from 95% alcohol 11.2 g. (63%) of γ-mannonic lactone melting at 151° was obtained.

Preparation from Ivory Nut Meal.—Six hundred grams of 20-mesh ivory nut meal was added to 6000 cc. of boiling 1% sodium hydroxide solution. The flame was removed before adding the meal. The mixture was allowed to stand with occasional stirring for thirty minutes and then filtered and washed with water until the washings were neutral and practically colorless.[6] The product was dried at 80°. The yield was 420 g.

One hundred grams of the purified meal was added in small portions and with constant stirring to 100 g. of cold 75% sulfuric acid and allowed to stand overnight. Eleven hundred cc. of water was added and the mixture boiled for three hours.[7] The hot solution was neutralized with barium carbonate, treated with decolorizing carbon and filtered. The filtrate was again treated with carbon and became practically colorless. Titration with iodine indicated the presence of about 90 g. (0.5 mole) of reducing hexose. The solution was diluted to 3750 cc. and cooled. Two hundred and eighty-

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[4] Fischer and Hirschberger, *Ber.*, 22, 3218 (1889).

[5] Hudson and Isbell, THIS JOURNAL, 51, 2225 (1929).

[6] Horton, *J. Ind. Eng. Chem.*, 13, 1040 (1921).

[7] Hudson and Sawyer, THIS JOURNAL, 39, 471 (1917).

five grams of barium benzoate was added and the mixture stirred until nearly all of the benzoate was dissolved. Thirty-one cc. of bromine was added and the flask shaken until all the bromine was in solution. The flask was set aside in a dark place for twenty-four hours. The precipitated benzoic acid was removed by filtration, the excess bromine by a stream of air and the barium by sulfuric acid. After filtration the solution was heated and treated with 140 g. of lead carbonate in aqueous suspension. After cooling and filtering the remaining bromide was removed with silver carbonate and the excess lead and silver precipitated with hydrogen sulfide. The insoluble sulfides were removed, the filtrate was heated with decolorizing carbon and evaporated under reduced pressure to 400 cc. The benzoic acid which had separated from solution was filtered off and that in solution was extracted with chloroform. Evaporation in *vacuo* was continued until the lactone suddenly precipitated in a solid crystalline mass. Enough 95% alcohol was added to dissolve all the lactone (hot). On cooling, the product crystallized. After filtering and drying it melted at 138–141°.

It was recrystallized from alcohol. Thirty-six grams of γ-mannonic lactone melting at 151° was obtained; $[\alpha]_D^{25}$ +51.3°. The physical constants of this substance as determined by Nef[s] are:' m. p. 151° and $[\alpha]_D^{20}$ +51.8°. On concentration of the combined mother liquors an additional 4 g. of pure lactone was recovered.

Summary

The method of oxidation of aldehyde sugars recently described by Hudson and Isbell applied to mannose has made possible the preparation of y-d-mannonic lactone in improved yield.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

FURTHER OBSERVATIONS ON THE INTERFERENCE OF NITRO GROUPS ON THE ZEREWITINOFF METHOD FOR THE QUANTITATIVE ESTIMATION OF ACTIVE HYDROGEN

BY HENRY GILMAN, R. E. FOTHERGILL AND E. B. TOWNE

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Introduction

Where there is no hydrogen there can be no active hydrogen.

Recently, Gilman and Fothergill[1] showed that nitro, nitroso and azo groups interfered with the Zerewitinoff method for the quantitative estimation of active hydrogen. Long years ago attention was directed by Hibbert and Sudborough[2] to abnormal results given by some nitro substituted compounds. They obtained slightly more than the calculated volume of gas (based on the one hydroxyl group) when *o*-nitrophenol was treated at room temperature with an amyl ether solution of methylmagnesium iodide. The volume of gas increased when the mixture was allowed to stand for an additional eight hours at room temperature.

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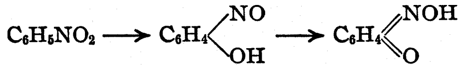
[8] Nef, Ann., 403, 316 (1914).

[1] Gilman and Fothergill, THIS JOURNAL, 49, 2815 (1927); 50, 867 (1928).

[2] Hibbert and Sudborough, J. *Chem. Soc.*, 85, 933 (1904).

Heating for twenty minutes at 115–120° caused the evolution of more gas, so that the total gas given off was almost twice that calculated for one active hydrogen.

They very correctly stated that "the high results obtained with *o*-nitrophenol appear to be due to the presence of the nitro group, as other nitro derivatives not containing hydroxyl groups, for example, *m*-dinitrobenzene, evolve a gas when mixed with methylmagnesium iodide, and the volume of gas is considerably increased when the mixture is heated." They suggested that this may be due to the nitro compound reacting as the tautomeric nitrosophenol or quinone-oxime, as follows



$$C_6H_5NO_2 \longrightarrow C_6H_4\left\langle\begin{matrix}NO\\OH\end{matrix}\right. \longrightarrow C_6H_4\left\langle\begin{matrix}NOH\\O\end{matrix}\right. \qquad (I)$$

This appears to be an altogether reasonable conjecture, and it has the merit of postulating two tautomeric forms each of which has an active hydrogen, namely, a hydrogen atom attached to oxygen. However, our studies on nitro[3] and nitroso[4] compounds have led us to the view that the interference of these groups is a property inherent in the nitro and nitroso groups, respectively. One way of finding a definite answer to this question is to determine the effect of a nitro group contained in a molecule free of hydrogen. This we have done. In the present study we have shown that tetranitromethane, $C(NO_2)_4$, and pentabromo-nitrobenzene, $C_6Br_5NO_2$, evolve considerable gas when treated with alkylmagnesium halides after the Zerewitinoff method for the quantitative estimation of active hydrogen. This proves that a phenolic or oximic or other active hydrogen grouping[5] is not necessary for the evolution of gas by a nitro compound. It does not prove, of course, that the tautomeric forms postulated in Reaction (I) are incorrect. However, our results do show that if the tautomeric phenolic and oximic forms of (I) are to have any claims to correctness they would rest on a more secure foundation on evidence other than that given by the reaction with alkylmagnesium halides.

Experimental Part

The several determinations were carried out in accordance with the procedure used by Gilman and Fothergill[1] in their earlier studies on nitro compounds. Methylmagnesium iodide was used with all compounds. The solvent, both for the Grignard reagent and the nitro compound, was *n*-butyl ether, excepting that the Grignard reagent for the tetranitromethane experiment was prepared in iso-amyl ether.

In a typical determination, 0.2497 g. of tetranitromethane when heated at 70°

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[3] Gilman and McCracken, THIS JOURNAL, 51, 821 (1929).

[4] Gilman and McCracken, *ibid.*, 49, 1052 (1927).

[5] By active hydrogen we mean here, in general, hydrogen attached to any element other than carbon, and in certain compounds of the latter class where, for example, the hydrogen is attached to a trebly bonded carbon of the acetylenic series.

for fifteen minutes gave 40.7 cc. of gas (measured under standard conditions). This is equivalent to 1.43 so-called "active hydrogens."

With pentabromo-nitrobenzene, 0.2552 g. of the compound when heated with methylmagnesium iodide at 70° for one and one-half hours gave 10.95 cc. of gas[6] (measured under standard conditions). This is equivalent to 0.99 so-called "active hydrogens." By way of reference, mention should be made of an experiment with pentabromobenzene, C_6HBr_5. When 0.2763 g. of this compound was heated at 70° for one-half hour, 0.35 cc. of gas was evolved. This is equivalent to 0.027 so-called "active hydrogens," and is within experimental error.

The pentabromo-nitrobenzene was prepared by the following reactions. First, *p*-nitro-aniline was brominated to 2,6-dibromo-4-nitro-aniline.[7] This was then diazotized and the amino group replaced by hydrogen to give 3,5-dibromonitrobenzene,[7] which was then reduced to 3,5-dibromo-aniline.[8] Bromination of the 3,5-dibromo-aniline gave the pentabromo-aniline,[9] from which the amino group was replaced by hydrogen by means of the diazo reaction to give pentabromobenzene.[10] The pentabromobenzene when nitrated gave the desired pentabromo-nitrobenzene, which melted at 230°. The melting point of our pentabromobenzene was 158–159°.

Summary

The interference of the nitro group in the Zerewitinoff method for the quantitative estimation of active hydrogen is an inherent property of the nitro group because gas is evolved from compounds such as tetranitromethane and pentabromo-nitrobenzene which contain no hydrogen.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE IRREVERSIBLE OXIDATION OF ORGANIC COMPOUNDS. IV.[1] THE OXIDATION OF ALDEHYDES

BY J. B. CONANT, J. G. ASTON AND C. O. TONGBERG

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The first two papers of this series[2] were concerned with the rate of oxidation of phenols and enols by strictly reversible oxidizing agents such as potassium ferricyanide. It was found that the speed of these irreversible oxidations was a function of the oxidation potential of the reagent and that the results could be formulated in terms of "apparent oxidation potentials."

In attempting to extend our methods to the study of the oxidation of aldehydes, we encountered surprising complications. A qualitative study[1]

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[6] Some halogen-nitro compounds like bromopicrin, when treated with methylmagnesium iodide evolve a mixture of gases, a part of which is methyl bromide.

[7] Meyer, Meyer and Taeger, *Ber.*, **53**, 2041 (1920).

[8] Holleman, *Rec. trav. chim.*, *25*, 194 (1906).

[9] Hantzsch and Smythe, *Ber.*, **33**, 520 (1900).

[10] Jacobson and Loeb, *ibid.*, **33**, 703 (1900).

[1] The third paper of this series was published in THIS JOURNAL, **50**, 2783 (1928), under the title "Certain New Oxidation Reactions of Aldehydes."

[2] Conant and Pratt, *ibid.*, 48, 3178, 3220 (1926).

of the action of a number of reversible oxidizing agents on aldehydes showed that the oxidation products were rarely the expected acids. Instead, the products were usually the result of a process of alpha oxidation, particularly if the reaction was carried out in a very dilute solution. For example, if ceric sulfate in sulfuric acid is employed, isobutyraldehyde is oxidized to the a-hydroxy-aldehyde; the same aldehyde with potassium ferricyanide in alkaline solutions yields a dihydropyrazine, presumably through the intermediate formation of an a-amino aldehyde, some of the nitrogen of the complex cyanide being transferred to the organic molecule. In the concluding portion of this present paper we are able to present conclusive evidence that a-amino compounds are formed by the oxidizing action of alkaline ferricyanide at elevated temperatures.

In spite of the complexity of the situation as revealed by the qualitative results, a quantitative study of the rates of oxidation has yielded quite definite results of considerable interest. Our electrochemical method of studying the rate of oxidation has been applied to the oxidation at 80° of a variety of aldehydes in acid solution using ceric sulfate and in alkaline or neutral solution using molybdicyanide, tungsticyanide and ferricyanide. On the whole, the results obtained with acid solutions and with alkaline solutions are consistent with the qualitative information, which showed that the primary reaction was the same under both sets of conditions and involved two equivalents of oxidizing reagent. In the following presentation of the quantitative results which we have obtained in the course of the last three years, we shall purposely avoid a detailed mathematical treatment of the data. Considering the complexity of the reaction which we are measuring, we can only hope to outline a first approximation to the final quantitative formulation.

The Rate of Oxidation in Acid Solution.—Since the object of this entire investigation was to examine the relationship between the rate of oxidation and the oxidation–reduction potential of the reagent employed, only those reagents could be used which are strictly reversible[3] and whose oxidation–reduction potential can be measured. Furthermore, since our experimental method of determining the rate of the reaction consists in noting the change of potential of the oxidizing mixture, only those reversible systems could be employed with which electrode equilibrium is established rapidly.

The ceric ion appears to be the only oxidizing agent which meets these specifications and which attacks aldehydes in acid solution at 80° at a measurable rate. The ferric ion and reagents of lower oxidizing potential are without effect; the action of the chromate ion is very slow and the system CrO_4^{--}–Cr^{+++} is not rapidly reversible. The action of potassium permanganate is too rapid and, as will be shown elsewhere, this reagent has

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[3] Conant, *Chem. Reviews*, 3, 1 (1926).

peculiarities of its own. The thallic–thallous system has a potential of 1.20 volts at 80° in 1 N sulfuric acid as compared with 1.42 for the ceric–cerous system and 0.71 for the ferrous–ferric. It would thus seem at first sight that the thallic ion would be a reversible oxidizing agent suitable for our study, particularly as acetaldehyde reduces it at 80° in 1 N sulfuric acid. Investigation, however, proved that the system was not rapidly reversible. Thus, although the ferric–ferrous system is 500 millivolts lower in potential, it takes more than a minute for an excess of thallic sulfate to oxidize ferrous sulfate in dilute solution to a point where ferrous ions can no longer be detected with ferricyanide. Similarly the characteristic yellow color of ceric sulfate is not discharged by an excess of thallous sulfate even on long standing, although there is a difference of about 200 millivolts representing the driving force of the reaction. The thallous–thallic system is clearly not sufficiently mobile to be of service. We were, therefore, confined to the use of one reagent, ceric sulfate.

The results obtained with ceric sulfate are summarized in Tables I and II. The apparatus and procedure were identical with those used in our previous work. The essential experimental facts are given in the footnote to Table I. The fraction of ceric sulfate (S) reduced at a given time was calculated from the change in potential (ΔE) of the electrode immersed in the reaction mixture, an equimolecular mixture of cerous and ceric sulfate being used in every experiment. The validity of this

$$\Delta E = 0.000198\ T \log \frac{1 + S}{1 - S} \qquad (1)$$

calculation was tested by adding definite amounts of ferrous sulfate solution to an equimolecular mixture of cerous and ceric sulfates. Each increment of ferrous ion produced a practically instantaneous drop in potential which corresponded within the experimental error of 1 millivolt to the change of potential calculated from Equation 1.

TABLE I

RATE OF OXIDATION OF ALDEHYDES AND GLUCOSE AT 80° IN 1 N SULFURIC ACID WITH CERIC SULFATE ($E_0' = 1.424$, PH, 0.37)

Concn. of reagent, moles, /liter × 10^3	Subs. oxidized	Concn. moles /liter × 10^3	Fraction (S) of reagent reduced in, minutes				$k \times 10^2$ Calcd. from S at, minutes				Average
			3	5	8	15	3	5	8	15	
2	Acetaldehyde	2	0.30	0.47	0.70	..	11.9	12.6	15.0	..	13.17
0.2	Acetaldehyde	0.2	.11	.21	.31	0.52	3.9	4.7	4.6	4.9	4.50
9.5	Acetaldehyde	9.5	.31	.53	.88	..	12.3	15.1	..	..	13.70
2	Propionaldehyde	2	.63	..	..	..	33.2	..	..	..	33.2
0.2	Propionaldehyde	0.2	.49	.76	..	..	22.4	28.5	..	..	25.4
2	n-Butyraldehyde	2	.50	.72	..	..	23.2	25.4	..	..	24.3
0.2	n-Butyraldehyde	0.2	.33	.54	..	..	13.4	15.5	..	..	14.5
2	*Iso*butyraldehyde	2	.83	..	..	..	59.0	..	..	..	59.0
2	Glucose	2	.24	.41	.61	.88	9.2	10.5	11.7	14.4	11.4
0.2	Glucose	0.2	..	..	.09	.18	..	..	1.2	1.3	1.25

NOTE.—In each experiment 100 cc. of 1 N sulfuric acid was placed in the cell and such amounts of ceric and cerous sulfate added (as 0.2 M solutions) as necessary to make an equimolecular mixture with the concentration of ceric ion given in Col. 1. The ceric sulfate was prepared by electrolytic oxidation of cerous sulfate and the concentration was determined by electrometric titration with ferrous ammonium sulfate. The temperature was 80 ± 0.5°. The aldehyde was added in a 0.2 M water solution in such amounts as to give the concentration noted in Col. 3; the time was recorded with a stop-watch. The potentials of the bright platinum electrodes (two were employed) were measured against a saturated calomel electrode at the same temperature. The potential of this calomel at 80° against a hydrogen electrode in 0.2 N hydrochloric acid at the same temperature was 0.253 which, corrected for vapor pressure, gives a value of 0.263 for 1 atm. of hydrogen. We have arbitrarily assumed the hydrogen-ion activity of hydrochloric acid to be independent of the temperature; therefore, the activity in 0.2 N hydrochloric acid is 0.76. Using this value and the measurement just mentioned, we assign the value of 3-0.210 volt to the calomel saturated electrode at 80° on the hydrogen scale. Using this value and measuring the hydrogen electrode in 1 N sulfuric acid at 80°, we find a PH value of 0.37. The ceric–cerous electrode against the saturated calomel was found to be 1.214 at 80°, thus giving a value of 1.424 for E_0' at 80°. This was the initial potential (±3 millivolts) in all the experiments listed above.

The values of the velocity constant given in Table I were calculated from the usual monomolecular Equation 2, the time being in minutes.

$$k = \frac{2.3}{t} \log \frac{1}{1 - S} \tag{2}$$

It is evident from an inspection of Table I that, in the case of the aldehydes, changing the concentration of the reactants affects the rate only slightly, which fact points to a rate-controlling step which is monomolecular. In the case of glucose the effect of dilution, however, is almost as much as would be predicted if a bimolecular process were involved. Since this work has been primarily concerned with aldehydes, we will leave to another paper a further consideration of the peculiarities of the glucose reaction. The data given in Table II show that lowering the temperature 20° decreases the rate of the reaction 3- to 4-fold.

TABLE II

RATE OF OXIDATION OF ALDEHYDES AND GLUCOSE AT 60° IN 1 *N* SULFURIC ACID WITH CERIC SULFATE

Concn. of reagents × 10^3	Sups. oxidized	Concn. moles /liter × 10^3	Fraction (*S*) of reagent reduced in, minutes				k × 10^2 Calcd. from *S* at, minutes				
			3	5	8	15	3	5	8	15	Average
2	Acetaldehyde	2	0.07	0.11	0.19	0.33	2.4	2.3	2.6	2.7	2.5
2	Propionaldehyde	2	.28	.45	.59	.83	11.0	12.0	11.1	11.8	11.5
2	n-Butyraldehyde	2	.16	.28	.43	.67	5.8	6.6	7.0	7.6	6.9
2	Isobutyraldehyde	2	.28	.44	.63	..	10.9	11.6	12.4	..	11.6
2	Glucose	2	..	..	..	.22	..	..	..	2.6	2.6

The potential of the ceric–cerous electrode at 60° was 1.200 against the saturated calomel at the same temperature.

The Rate of Oxidation in **Alkaline** Solution.—The only oxidizing agents which we have been able to employ in neutral or alkaline solution are the complex cyanides of iron, tungsten and molybdenum which were used in our previous papers. Such reagents as Tollens' solution and Fehling's solution are not reversible oxidizing agents and none of the quinones or dyes which have been investigated are sufficiently powerful oxidizing agents to attack aldehydes in dilute solution even at 80°.

The data in Table 111 show the effect of dilution on the rate of the reaction. In the case of the aldehydes (Section A), the reaction is clearly of the second order and the values of k_2 have been calculated from Equation **3.** With glucose and the naphthols (which are included for purposes

$$k_2 = \frac{1}{tC} \times \frac{S}{1 - S} \qquad (3)$$

of comparison) the rate of the reaction is more nearly independent of the dilution and the values of k given are those calculated by means of the first-order equation.

TABLE III

EFFECT OF DILUTION ON THE RATE OF OXIDATION OF CERTAIN SUBSTANCES AT 80°. REAGENT, POTASSIUM FERRICYANIDE

PH	Concn. of reagent, moles per liter X 10^3	Subs. oxidized	Concn., moles per liter X 10^3	Fraction (S) of reagent reduced in, minutes 5	15	30	k_2 calcd. from S at minutes 5	15	30
		(A) Aldehydes (Second-order reaction)							
10.75	1.83	Acetaldehyde	1.83	0.10	0.30	0.51	12	16	19
10.75	9.17	Acetaldehyde	9.15	.32	.70	> .9	10	17	...
8.6	1.91	Propionaldehyde	1.91	.21	.52	.70	28	38	41
8.6	9.55	Propionaldehyde	9.55	.68	.89	..	44	56	...
9.0	1.91	n-Butyraldehyde	1.91	.35	.68	.83	58	73	84
9.0	9.17	n-Butyraldehyde	9.55	.76	.9	> .9	69	...	...
7.5	1.91	Isobutyraldehyde	1.91	< .1	.21	.38	..	9.4	10
7.5	9.17	Isobutyraldehyde	9.55	.16	.47	.76	4.1	6.5	11
9.0	1.91	Acrolein	1.91	.08	.32	.51	9	16	18
9.0	9.17	Acrolein	9.55	.32	.71	> .9	10	18	...
		(B) Sugar and naphthols (Essentially first-order reaction)							
9.0	2	d-Glucose	2	0.05	..	0.39			
9.0	10	d-Glucose	10	.09	..	.47			
9.0	2	d-Fructose	10	.08	..	.65	1.7	3.5	...
9.0	10	d-Fructose	10	.12	..	.64	2.5	3.4	...
5.3	1.93	α-Naphthol	1.93	.16	.33	.46	3.5	2.8	2.1
6.3	9.6	a-Naphthol	9.6	.30	.53	.64	7.2	5.0	3.4
7.5	1.93	β-Naphthol	1.93	.06	.13	.25	1.2	.92	.96
7.5	9.6	β-Naphthol	9.6	.14	.35	.49	3.0	2.9	2.2

In each experiment 100 cc. of buffer solution was placed in the cell and **after it** had come to temperature equilibrium in the thermostat, 2 cc. each of a solution of oxidized and reduced forms of reagent were added; the resulting concentrations were those in Col. 2. After waiting for ten minutes (to allow for temperature readjustment), a 0.2 molar solution of tho aldehyde was added in such amount that the concentration of the cell was that given in Col. 4. The naphthols were added as solids.

As in the case of the oxidation of phenols and enols, the rate of oxidation of aldehydes by the complex cyanides is a function of the alkalinity of the solution. The more alkaline the solution the more rapid the reaction. In this connection it must be remembered that the potential of the complex cyanides (unlike the quinones) is practically constant from PH values 3–12. We have determined the PH at which each aldehyde is just appreciably oxidized by (a) ferricyanide, (b) tungsticyanide, (c) molybdicyanide. The data are summarized in Table IV.

TABLE IV

THE RATE OF OXIDATION OF CERTAIN ALDEHYDES AT 80 ± 0.2° IN DIFFERENT BUFFER SOLUTIONS 0.002 M WITH RESPECT TO SUBSTANCE AND REAGENT. F = POTASSIUM FERRICYANIDE; M = POTASSIUM MOLYBDICYANIDE; T = POTASSIUM TUNGSTICYANIDE

Substance	Re-agent	PH of soln.	E_0' of reagent	Fraction re-acted (S) in minutes 5	30	Reaction constant (first-order reaction) k × 10^2 calcd. at 5 min.	30 min.	Average	App. oxid. potential
Formaldehyde	F	10.9	0.296	< 0.1	< 0.1	..	..	...	...
	M	10.9	.647	.12	.68	2.6	3.8	3.2	0.593
	M	104	.647	< .1	.13	..	0.9	0.9	.648
Acetaldehyde	F	10.9	,292	.16	.73	3.5	4.4	4 0	.228
	F	10.4	.302	.06	.26	1.2	1.0	1.1	.298
	T	10.4	.408	.40	> .9	10.2	.	10.2	.301
	T	9.0	.432	.10	.39	2.1	1.7	1.9	.402
	M	7.5	.669	.12	.69	2.6	3.9	3.2	.615
	M	6.8	.650	< .1	.12	..	0.43	0.43	.717
Propionaldehyde	F	9.0	.322	.47	.87	12.7	6 8	10 2	.214
	F	8.2	.324	< .05	.40	,	1.7	1 7	.300
	T	8.2	.431	.59	> .9	17 8	..	17.8	.299
	T	7.5	.424	.17	.74	3.7	4.5	4.1	.359
	M	6.1	.670	.19	> .9	4.2	..	4.2	.604
	M	5 4	,680	< .05	.13	..	0.5	0.5	.712
Isobutyraldehyde	F	8.2	.321	.09	.72	1.9	4.2	3.2	.268
	F	7.5	,310	< .1	.38	1.7	1.6	1.7	.286
	T	6.8	.424	.08	.53	1.7	2.5	2.1	.390
	T	6.1	.433	< .05	.23	..	0.87	0.87	.440
	M	6.1	.674	.1	> .9	2.1	..	2.1	(.602)
	M	5.4	.681	< .05	.13	..	0.5	0.5	.703
n-Butyraldehyde	F	8.2	.325	< .05	.18	..	.73	0.73	.301
	F	9.0	.319	.35	.83	8.6	5.9	7 2	.228
	T	7.5	.423	.13	.71	2.8	4.1	3.5	.366
	T	8.2	.431	.56	> .9	16.4	..	16.4	.303
	M	6.1	.673	.21	> .9	4.7	..	4.7	.602
	M	5.4	.681	< .1	< .1	..	..	...	..
Acrolein	F	9.0	.319	.08	.51	1.7	2.4	2.1	
	F	8.6	.320	< .1	.32	..	1.3	1 3	
	M	6.1	.668	.07	..	1.5	..	1.5	
	M	5.4	.668	< .1	< .1	..	..	...	

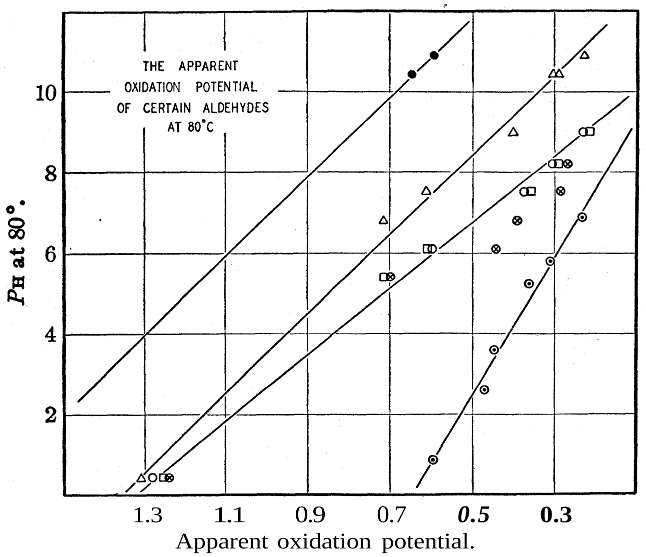
NOTE.—The experiments recorded in the above table were all performed in duplicate. The results agreed within 20% (expressed as fraction reacted in a given time). To save space only one determination has been recorded and the 15-minute values of *S* and ks have been omitted, but were included in the average value of ks used in calculating the apparent oxidation potential. With most of the compounds many experiments in other buffer solutions were carried out, in which the rates were too fast or too slow to give significant values for ks. All these results were consistent with our electrochemical formulation. The following experimental details are to be noted in connection with the above data. The hydrogen electrode (corrected for vapor pressure) in 0.2 *N* hydrochloric acid was taken as the standard of potential at 80°. It was arbitrarily assumed that the activity of the hydrogen ion at this temperature in this solution was 0.76 (the value at 25°). On this basis the hydrogen electrode in 0.2 N hydrochloric acid was given the value of —0.053 at 80°. The particular saturated calomel electrode used as a working standard at 80° had a value of +0.225 on this basis; this value was repeatedly checked. The normal potentials of the reagents were determined at 80° against this calomel electrode. The PH of the buffer solutions at 80° was determined directly with the hydrogen electrode. All the buffer solutions were 0.2 molar with respect to the buffering ion and were made up to an ionic strength of 0.6 with appropriate amounts of sodium chloride. The materials used in preparing the various solutions were as follows: *PH* 5.3, sodium acetate and acetic acid (molybdicyanide potentials showed an abnormally large "drift" in acetate buffers and they were not employed with this reagent); *PH* 5.4, 6.1, 6.8, potassium dihydrogen phosphate and sodium hydroxide; *PH* 8.2, 8.6, 9.0; *PH* 10.4, 10.75, 10.9, secondary and tertiary sodium phosphates.

The most convenient method of summarizing the behavior of aldehydes toward reversible oxidizing agents is by formulating the results in terms of "apparent oxidation potentials." This method has been developed and used in previous papers. In this instance it is more difficult to apply because the rate of oxidation in alkaline solution is so dependent on the dilution. In spite of this complication a fairly satisfactory picture of the process may be developed by confining the attention to one concentration (0.002 M) and in the case of the results with both ceric sulfate and the complex cyanides calculating the rate constant from the monomolecular formula. The apparent oxidation potential is then defined as the potential of the reagent which will just bring about the oxidation at the rate $k = 0.01$ at 80° and the *PH* specified. The rate constants given in Table IV are the *first* order *constants.* Since it rarely happens that $k = 0.01$ in any actual experiment, an interpolation between two values is necessary (or sometimes an extrapolation). In a few cases it was possible to measure the rate of oxidation of a given aldehyde with two reagents in the same buffer. The results of these experiments show that consistent values of the apparent oxidation potential are obtained by using Equation 4, which is of the usual form but contains the quite empirical factor 0.003 T (instead of the usual 0.002 T or 0.001 T).

$$\text{Apparent oxidation potential} = E_0' \text{ (of reagent)} + 0.003\ T \log \frac{0.01}{k} \qquad (4)$$

The values of the apparent oxidation potential given in Table IV and plotted in Pig. 1 were thus calculated using the average value of k. The success of the empirical equation in representing the data is shown by the calculation of apparent oxidation potential of acetaldehyde at PH = 10.4, propionaldehyde PH = 8.2, and n-butyraldehyde at *P*H = 8.2. The two values in each case calculated from the results with two reagents agree within a few millivolts.

The general consistency of the results is also shown by Pig. 1. The results at *P*H 0.37 were calculated from the data in Table I using Equation 4; they are as follows: acetaldehyde, apparent oxidation potential = 1.307; propionaldehyde, 1.252; n-butyraldehyde, 1.278; *iso*butyraldehyde, 1.236. It should be noted that formaldehyde is not appreciably attacked by ceric sulfate, a fact which fits perfectly with the results at PH 11. For the purposes of comparison the results with a-naphthol and 8-naphthol are included. Some of these are new measurements (Table VI) and some from a previous paper. The best straight line has been drawn through the formaldehyde, acetaldehyde and the *n*-butyraldehyde points; n-propionaldehyde is indistinguishable from *n*-butyraldehyde. The isobutyraldehyde values are the most irregular. It is quite clear that the data obtained in acid solution with ceric sulfate are part of the general picture. The position of the points in alkaline and



●, Formaldehyde; □, propionaldehyde; ⊗, isobutyraldehyde; A, acetaldehyde; O, n-butyraldehyde; ⊙, 8-naphthol at 60° (from previous work).

Fig. 1.—The apparent oxidation potential of certain aldehydes at 80°.

neutral solution would have led to the prediction of the apparent osidation potential at PH = 0.37 within at least 100 millivolts.

TABLE V

RATE OF OXIDATION OF FORMALDEHYDE AND ACETALDEHYDE AT 60 ± 0.2° IN DIFFERENT BUFFER SOLUTIONS 0.002 M WITH RESPECT TO THE SUBSTANCE AND REAGENT. F = POTASSIUM FERRICYANIDE; M = POTASSIUM MOLYBDICYANIDE

Substance	Reagent	PA of soln.	E_0' of reagent	Fraction reacted (S) in minutes 5	30	Reaction constant (first order) $k \times 10^2$, in minutes 5	30
Formaldehyde	F	12.0	0.345	< 0.1	< 0.1	..	..
	M	12.0	.646	.4	$>$ .9	10	..
	M	11.2	.666	$<$ .1	.12	..	0.43
Acetaldehyde	F	11.2	.348	$<$ .1	.14	..	0.51
	F	12.0	.347	.28	.89	6.5	7.4
	M	9.2	.663	.34	$>$ .9	8.3	..
	M	8.4	.665	$<$ .1	.24	..	0.88

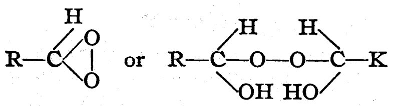
TABLE VI

DETERMINATION OF APPARENT OXIDATION POTENTIAL OF a- AND β-NAPHTHOLS AT 80 ± 0.2° IN DIFFERENT BUFFER SOLUTIONS 0.002 *M* WITH RESPECT TO SUBSTANCE AND REAGENT. F = POTASSIUM FERRICYANIDE

Substance	Reagent	PA of soln.	E_0' of reagent	Fraction reacted (S) in 5 min.	30 min.	Reaction constant $k \times 10^2$ 5 min.	30 min.	App. oxid. potential, volt
α-Naphthol	F	8.2	0.324	0.9	0.9	..	..	...
	F	6.12	.322	.71	.9	25	..	0.231
	F	5.36	.325	.25	.60	5.7	3.1	.281
	F	5.26	.330	.16	.46	3.5	2.1	.299
β-Naphthol	F	8.2	.324	.45	.78	12.0	5.0	.261
	F	7.5	.313	.06	.25	1.2	.96	.312

Discussion of Results

While Equation **4** and Fig. **1** are a satisfactory empirical formulation of the results, interpretation of them in terms of a simple mechanism does not seem possible. The slope of the PH–apparent oxidation potential line corresponds approximately to 0.003 T. This is in marked contrast to the oxidations of enols and phenols, where in almost every case the slope is 0.0002 T, the apparent oxidation potential curve paralleling the line for the hydrogen electrode. The contrast between the behavior of aldehydes and the naphthols is clear from Fig. 1. Since the rate of the oxidation of aldehydes by reversible reagents (at 80° in dilute solutions) seems to be a regular function of the potential of the reagent and the *P*H of the solution, this reaction must be classified with those oxidations which may be formulated on an electrochemical basis. For the reasons given elsewhere[3] it seems that in all such processes there is a reversible step followed by a slow irreversible rate-controlling reaction. We are inclined to believe that the reversible step in the case at hand involves the formation of a peroxide of the types



or a free radical from the hydrated form of the aldehyde. The abnormal slope of the apparent oxidation potential–PH curve might be due to hydroxyl-ion catalysis of the irreversible step. The apparent second order reaction with the complex cyanides may be due to the interaction of the first product and the cyanide with the formation of the dihydropyrazine. We have not been able, however, to devise a combination of any such mechanisms which will lead to the quantitative relationships actually found. Considering the complexities revealed by the qualitative study of the reactions, it is perhaps not surprising that the quantitative results defy analysis.

In considering Fig. 1 as a description of the oxidation of aldehydes at 80° in dilute solution, several points must be kept in mind. The curves refer to one concentration (0.002 M); in more concentrated solution the apparent oxidation potential would be lowered, in more dilute solutions raised, at least in the alkaline solutions. Judging from the results of Table III, the effect would be about 100 millivolts for each 10-fold change. The acid points would also be changed by change in concentration, since it is clear from Table I that there is a change of rate with change of concentration, though it is less than when ferricyanide is used. The effect of change in temperature is complicated because of the change of the PH value, the potential of the reagent and the rate of the oxidation. At temperatures near 80° the increase in the apparent oxidation potential of 80 to 100 millivolts for a 20° lowering of temperature would be expected from the data in Tables II and V. At 25° the aldehydes are only attacked by molybdicyanide in extremely alkaline solution.

The process or processes which are involved in the reaction which we have attempted to formulate in Fig. 1 involve the oxidation of the aldehyde in the a-position. The so-called "normal" oxidation of aldehydes to acids is another story. In this connection the action of two common reagents—Fehling's solution and Tollens' solution—is of interest. In neither of these reagents is there a mobile equilibrium between the oxidized and reduced form. According to our views, their action would therefore not be expected to fit into the electrochemical picture. That this is the case is shown by the fact that rough estimations of the rate of reduction of Fehling's solution at 80° gives the order: acetaldehyde > a- and 8-naphthol > formaldehyde. Tollens' reagent at room temperature gives the order, formaldehyde > acetaldehyde > α-naphthol > @-

naphthol. Ammoniacal silver nitrate at 80° shows the following: formaldehyde and the naphthols instantaneous action, acetaldehyde much slower. The predicted speed of oxidation by reversible reagents from Fig. 1 is a-naphthol > β-naphthol > acetaldehyde > formaldehyde; this does not correspond with that found with any of the reagents just mentioned. It seems probable that in the case of the oxidation of aldehydes with the complex metal positive ions, an addition compound is first formed. The formation of such a compound and its rate of decomposition would not be expected to be a function of the oxidation–reduction potential of the reagent. It might further be noted that it is extremely probable that the chief product of the oxidation of aldehydes by cupric and silver hydroxide and their complexes is in every case the corresponding acid.

Further Evidence Concerning the Nature of the Product.—Except in a few cases, the process of a-oxidation does not stop with the formation of the hydroxy-aldehyde but proceeds further. This was made evident by the results published in the last paper. We have obtained further evidence on this point by determining the number of equivalents of ferricyanide or of ceric sulfate which are required for complete oxidation of a few aldehydes and sugars. The general procedure was to add an excess of reagent together with its reduced form and follow the change of potential with time. The rate of change of potential, which was at first rapid, gradually decreased until after two or three hours there was no appreciable change; this was taken as the end of the reaction. The total change of potential is a measure of the amount of oxidizing agent which has been reduced. A few typical results obtained using ceric sulfate are given in Table VII. A test of the method is given by the results with oxalic acid in which two equivalents must almost necessarily be involved.

TABLE VII

DETERMINATION OF THE NUMBER OF EQUIVALENTS INVOLVED IN THE OXIDATION OF CERTAIN COMPOUNDS BY CERIC SULFATE IN 1 N SULFURIC ACID AT 80°.

TYPICAL RESULTS

Substance	Time, min.	*AB*, mv.	*S*	Equivalents
Oxalic acid,	0	0	0	
concn., 0.008	1	74	0.84	
mole per liter	14	74	.84	2.1
Isobutyraldehyde,	0	0	0	
concn., 0.001	65	56	.72	
mole per liter	88	60	.76	
	100	61	.77	
	126	64	.78	1.6

Where the number of equivalents is large the results are less certain and may be in error in the case of glucose, for example, by one or two equivalents. The following results have been obtained, all at 80°.

Substance and reagent	No. of equivalents
Acetaldehyde with ferricyanide (P_H 10.8)	1.9
Acetaldehyde with ceric sulfate (P_H 0.37)	2.5
Propionaldehyde with ferricyanide (P_H 10.8)	2.6
n-Butyraldehyde with ferricyanide (P_H 10.9)	at least 5
n-Butyraldehyde with ceric sulfate (P_H 0.37)	4
Isobutyraldehyde with ferricyanide (P_H 10.9)	2
Isobutyraldehyde with ceric sulfate (P_H 0.37)	1.6–3.0
d-Glucose with ferricyanide (P_H 10.4)	12.2
d-Glucose with ceric sulfate (P_H 0.37)	8.8
d-Fructose with ferricyanide (P_H 10.4)	11.2
d-Arabinose with ferricyanide (P_H 10.4)	7.5

The oxidation of d-glucose by both ferricyanide and ceric sulfate is probably complete, since a determination of the amount of carbon dioxide evolved using ceric sulfate showed 6 moles per mole of sugar; the value of the number of equivalents obtained with this reagent is therefore probably below the true value.

In the previous paper the formation of dihydropyrazine derivatives by the action of potassium ferricyanide on aldehydes and ketones was explained by the assumption that the a-amino compound was first formed and then underwent condensation. We have been able now to demonstrate the correctness of this mechanism, at least in the case of ketones. Gabriel[4] has shown that a-aminophenyl isopropyl ketone, unlike most a-amino ketones, does not condense to a dihydropyrazine. We therefore oxidized phenyl *iso*propyl ketone with ferricyanide according to our usual procedure and obtained the a-amino compound. The yield was small and all attempts to change the conditions to obtain a better yield failed. The method therefore does not appear very suitable for the preparation of this compound. The experimental details are given below.

A solution of 58 g. of potassium ferricyanide in 500 cc. of water was heated to 85–95' and 10.4 g. of phenyl isopropyl ketone and 200 cc. of 2 N sodium hydroxide was added. The hydroxide was added gradually and finally 25 cc. of 5 *N* sodium hydroxide was introduced. The characteristic red precipitate of ferric hydroxide formed rapidly. After thirty minutes the solution was cooled, filtered and extracted with chloroform. The basic material was extracted from the chloroform with dilute hydrochloric acid, then liberated by the addition of alkali and extracted with chloroform. On distillation 0.5 g. of α-aminophenyl isopropyl ketone was obtained (b. p. 247–257°, hydrochloride m. p. 187–188° after recrystallization from acetoacetic ester).

Evidence of the formation of a-aminomethyl isopropyl ketone was also obtained in some experiments conducted with methyl isopropyl ketone. The reaction mixture, obtained in the usual way, was filtered from the iron oxide, acidified with acetic acid and evaporated at 40° under diminished pressure to a small volume. The solution was then made strongly alkaline and stirred with benzene sulfone chloride for four hours. On working up the reaction mixture in the usual way, 1 g. of a white crystalline solid was obtained which was evidently the benzenesulfone derivative of the α-amino

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[4] Gabriel, *Ber.*, 44, 60 (1911).

ketone. It melted at 93.5–94.5° after recrystallization from hot water. It was soluble in alkali but insoluble in acid; it contained nitrogen and sulfur.

Anal. Calcd. for $C_{11}H_{15}NSO_3$: C, 54.7; H, 6.3. Found: C, 53.9; H, 6.6. Mol. wt. in camphor (micro method): 255. Calcd.: 241.

In connection with the quantitative results reported in the first portion of this paper, it should be mentioned that a study was made of the action of molybdicyanide on *iso*butyraldehyde at 80° in a phosphate buffer. No evidence of the formation of acetone could be obtained. The distillate gave the test for the α-hydroxy*iso*butyraldehyde (see experimental portion of previous paper) but only in the first 30 cc. The amount of this found is therefore slight. The reaction mixture, also, did not give the characteristic precipitate of the dihydropyrazine perbromide when treated with bromine. However, after making alkaline, heating and reacidifying, the addition of bromine yielded a precipitate of what appeared to be the perbromide of the dihydropyrazine. It thus appears that with molybdicyanide as with ferricyanide the oxidation product is the a-amino aldehyde.

Summary

1. The rate of oxidation of a number of aldehydes at 80° in 1 *N* sulfuric acid by ceric sulfate has been measured.

2. The rate of oxidation of certain aldehydes at 80° in alkaline and neutral buffer solutions by ferricyanide, tungsticyanide and molybdicyanide has been determined.

3. A comparison of the results obtained at the different acidities shows that the reaction between aldehydes and reversible oxidizing agents can be formulated in electrochemical terms. The equations necessary to describe the change of rate with change in acidity (P_H) and change of potential of the reagent, however, contain factors which do not correspond to any simple mechanism.

4. The action of Fehling's solution, ammoaiacal silver nitrate and Tollens' reagent are quantitatively different from the action of the reversible reagents.

5. a-Aminophenyl *iso*propyl ketone has been isolated from the products obtained by the oxidation of phenyl *iso*propyl ketone by ferricyanide.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION NO. 183 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

A STUDY OF THE PREPARATION AND PROPERTIES OF VITAMIN C FRACTIONS FROM LEMON JUICE[1]

BY H. L. SIPPLE AND C. G. KING

RECEIVED AUGUST 26, 1929 PUBLISHED JANUARY 8, 1930

Vitamin C fractions from lemon juice have been studied by Zilva and co-workers,[2] and Bezssonov has investigated the antiscorbutic vitamin as obtained from such sources as cabbage juice and potatoes.[3] However, very little is known as yet regarding the constitution of Vitamin C. It is probably the least stable of the vitamins and accordingly has been studied very little from a chemical point of view. This investigation of the preparation and properties of antiscorbutic fractions from lemon juice has been carried out in cognizance of the fact that such a study might furnish further information leading toward the isolation of Vitamin C.

Experimental

The general procedure used in testing the various fractions was the method which has been described by Sherman and co-workers.[4]

The guinea pigs used for testing the preparations were fed daily doses which were known to be equivalent to a certain volume of original lemon juice. The test period used was generally fifty-six days.

In order to avoid inactivation of the vitamin, all laboratory operations were carried out rapidly, under nitrogen gas, at relatively low temperatures, and in acid solution if possible. Fresh preparations were made each week. All fractions were stored under nitrogen in tightly stoppered bottles kept in a refrigerator. The liquids fed were always water solutions, free from toxic substances such as alcohols, ethers, heavy metals or appreciable amounts of acids.

Preparation of Vitamin C Fractions

Preparation I.—Lemon juice was decitrated with an excess of neutral lead acetate solution, the lead being removed from the remaining solution

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[1] This paper is based upon a thesis presented to the Graduate School of the University of Pittsburgh by Mr. H. L. Sipple in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] S. S. Zilva, *Biochem. J.*, **22**, 779 (1928); *ibid.*, **21**, 354, 689 (1927); *ibid.*, **19**, 589 (1925); *ibid.*, **18**, 182, 632 (1924); *ibid.*, **17**, 410 (1923); *ibid.*, **16**, 42 (1922); S. J. B. Connell and S. S. Zilva, *ibid.*, **18**, 638, 641 (1924); A. Harden and S. S. Zilva, *ibid.*, **12**, 93 (1918).

[3] N. Bezssonov, *ibid.*, **17**, 420 (1921); *Compt. rend.*, **186**, 259 (1928); *ibid.*, **180**, 970 (1925); *Bull. soc. chim. biol.*, **9**, 578 (1927).

[4] H. C. Sherman, "Chemistry of Food and Nutrition," **1926**, The Macmillan Co., New York, 3d ed., p. 424; H. C. Sherman, V. K. La Mer and H. L. Campbell, THIS JOURNAL, **44**, 165 (1922).

by precipitation with 10% phosphoric acid solution. After concentration in *vacuo* below 50°, the liquid was treated with two volumes of alcohol and filtered. The alcohol was removed from the filtrate by vacuum evaporation, the residual concentrate diluted with distilled water to one-half the equivalent volume of lemon juice, and fed to guinea pigs. Table **I** clearly indicates that no appreciable loss in Vitamin C content occurred in this treatment.

TABLE I

TEST DATA ON PREPARATION I

Lemon juice equivalent fed daily, cc.	Number of animals	Average survival (56-day test)	Average scurvy score	Average gain in weight, g.
Lemon juice, **1.5**	2	56	0	151
Decitrated lemon juice, **1.5**	2	56	0	169
Decitrated lemon juice, **3.0**	2	56	0	155
0	2	26	15	−68

Preparation II.—Decitrated lemon juice containing an excess of lead acetate was treated with dilute ammonium hydroxide until the *P*H was brought to 7.4–7.6 (phenol red). The yellow precipitate which formed was quickly centrifuged and the supernatant liquid decanted. The precipitate was dissolved in dilute acetic acid and dilute ammonium hydroxide added until the solution was brought to **a** PH of 7.4–7.6. The yellow precipitate was again centrifuged and dissolved in dilute acetic acid. The lead was removed from all fractions by precipitation with 10% phosphoric acid solution.

The results of feeding the various fractions of Preparation II appear in Table II. Both the first and second precipitates retain the vitamin with but slight loss in potency. Reprecipitation can evidently be employed as a further step in the purification since the first precipitate, as fed, contained 6.72 mg. of total solids per cc. of lemon juice equivalent while the second precipitate fraction contained 4.45 mg. of solids per cc. of lemon juice equivalent.

TABLE II

TEST DATA ON PREPARATION II

Lemon juice equivalent fed daily, cc.	Number of animals	Average survival (56-day test)	Average scurvy score	Average gain in weight, *g*.
Filtrate from first active ppt., **1.5**	3	26	21	−83
Filtrate from second active ppt., **1.5**	3	23	18	−87
First act. ppt., **1.5**	2	56	tr.	10
First act. ppt., **3.0**	2	56	0	113
Second act. ppt., **1.5**	3	56	8	12
Second act. **ppt., 3.0**	2	56	tr.	50
Lemon juice, **1.5**	2	56	0	189
0	2	22	19	−72

Preparation 111.—Continuing the purification of Preparation II, an aqueous solution of the material from the second active precipitate (lead free) was treated with two successive portions of n-butyl alcohol, the alcohol being drawn off each time. The butyl alcohol removed practically all of the yellow coloring matter from the aqueous solution, leaving the vitamin in the water phase (Table 111), showing that Vitamin C is not closely associated with the bulk of the yellow coloring matter, and that the vitamin is much more soluble in water than in n-butyl alcohol. This does not necessarily indicate that Vitamin C is insoluble in n-butyl alcohol.

TABLE III

TEST DATA ON PREPARATION III

Lemon juice equivalent fed daily, cc.	Number of animals	Average survival (56-day test)	Average scurvy score	Average gain in weight, g.
Lemon juice, 1.0	2	56	0	178
Aqueous fraction, 1.0	3	56	7	41
Aqueous fraction, 2.0	3	56	tr.	70
Butyl alc. fraction, 1	5	30	19	−127
Butyl alc. fraction, 2	5	29	18	−112
0	2	27	17	−97

Preparation IV.—The solid material obtained from an active aqueous fraction prepared as in Preparation III was dissolved in 98% alcohol and the solution treated with one volume of peroxide-free absolute ethyl ether. The white crystalline precipitate (principally ammonium salts) which formed was centrifuged and the supernatant yellow liquid decanted. Table IV shows that in this preparation the vitamin remained in the liquid phase.

TABLE IV

TEST DATA ON PREPARATION IV

Lemon juice equivalent fed daily, cc.	Number of animals	Average survival (49-day test)	Average scurvy score	Average gain in weight, g.
Positive controls, second act. ppt., 1	2	49	tr.	83
Solid phase, 2	5	25	18	−75
Liquid phase, 2	6	49	0	90
Both phases, 2 **cc. each**	5	49	0	100
0	3	20	15	−69

Upon analysis the ether–alcohol liquid was found to contain 0.56 mg. of total solids per cc. of equivalent lemon juice. The ash was inappreciable. Reducing substances (Munson–Walker method) calculated as glucose gave a value of 0.45 mg. per cc. The ammonium salts present were found, by steam distillation from alkaline solution, to be 0.045 mg. per cc. expressed as nitrogen. The total nitrogen as determined by the micro-Kjeldahl method was 0.145 mg. of N per cc. The acidity of the total solids was equivalent to 0.39 cc. of 0.01 N NaOH per cc. The ferric chloride test for phenolic bodies was negative. Ammoniacal silver nitrate was reduced slightly in the cold. An osazone reaction indicated glucosazone by its crystal form. A mildly positive carbylamine reaction was obtained, which might have been due to the interaction of sugars and ammonium salts present.

Barium Acetate and Sodium Hydroxide as Precipitating Reagents.—The precipitation of the vitamin by lead at a P_H of 7.4–7.6 seems to be a more or less specific adsorption phenomenon and not dependent upon the hydrogen-ion concentration alone. This was indicated by the results of substituting barium acetate for lead acetate or sodium hydroxide for ammonium hydroxide in making vitamin precipitations.

When barium acetate was substituted for neutral lead acetate in the precipitation procedure, the procedure being unchanged otherwise, a yellow precipitate formed at the usual P_H (7.4–7.6) but it did not remove the antiscorbutic factor from solution. The filtrate proved to be nearly as active as the original lemon juice.

In another experiment dilute sodium hydroxide solution was substituted for ammonium hydroxide in making the basic lead acetate precipitation, care being taken to make the precipitation in the customary P_H range of 7.4–7.6. It was found that the antiscorbutic material was not precipitated and that the treatment caused some inactivation of the vitamin.

Extraction with Absolute Ether.—The highly purified active alcohol–ether preparation of Vitamin C described above was evaporated to dryness in *vacuo,* and the residue extracted with absolute ether. The vitamin was not extracted from the solid material by the absolute ether, but a significant amount of amorphous material was removed by the ether, which would not redissolve in water. This left the total solids of the active fraction equivalent to 0.28 mg. per cc. of lemon juice.

Conclusions and Summary

Lemon juice has been decitrated by the addition of an excess of neutral lead acetate, and a lead complex containing practically all of the Vitamin C has been precipitated from the resulting liquid at a P_H of 7.4–7.6 by the addition of dilute ammonium hydroxide. This active complex has been reprecipitated, effecting a decrease in the total solids without appreciable loss of the vitamin. Barium acetate or sodium hydroxide could not be substituted for lead acetate or ammonium hydroxide in the precipitation of the vitamin. Absolute ethyl ether precipitated white crystalline inactive material, principally ammonium salts, from alcoholic solution of a highly purified vitamin preparation without precipitating the vitamin. Absolute ethyl ether did not extract Vitamin C from the solid material obtained by evaporation of the active alcohol–ether fraction. The total solids per cc. of lemon juice has been reduced from approximately 100 mg. in the original juice to 0.28 mg. for the final active preparations. The solid material in the final active fraction was chiefly carbohydrate in nature. The removal of inactive material has been accomplished without a great loss of the original Vitamin C content.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

STUDIES IN THE CYCLOPROPANE SERIES.
XII. NITROCYCLOPROPANES

BY E. P. KOHLER AND S. F. DARLING

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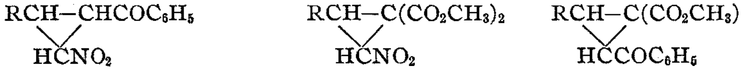
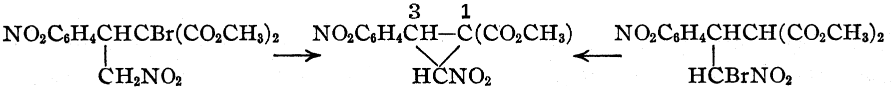
The manner in which bases convert derivatives of nitrocyclopropane into open-chained compounds is still obscure because each type of derivative that has been studied has ended in a different type of open chained compound, and it has not been possible to isolate intermediates in the process. In the hope of discovering such intermediates we have prepared still another type of derivative which is closely related to two that have been studied heretofore



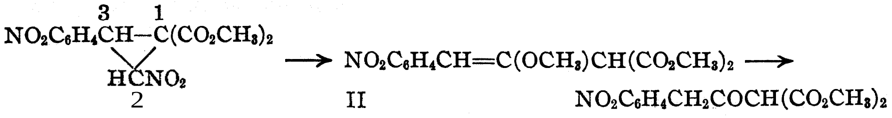
A B C

In order to keep as close as possible to known substances, we planned to prepare a nitrocyclopropane derivative of the type represented by B in which the hydrocarbon residue was to be a phenyl group; but owing to experimental difficulties, it became necessary to secure greater crystallizing power by resorting to substances in which the phenyl groups were substituted. Most of our experiments were carried out, therefore, with the m-nitrophenyl derivative.

The fact that our parent substance was obtained both from an α-bromo and from a γ-bromo compound is adequate proof that it is a cyclopropane derivative

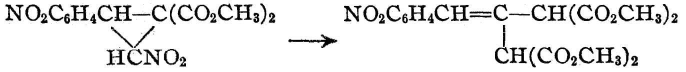


When this cyclopropane derivative is heated with methyl alcoholic potassium acetate—a very feeble base—it is slowly converted into a yellow methoxy compound. The structure of this yellow product was easily established. Its composition and molecular weight are represented by the formula $C_{14}H_{15}O_7N$. It is actively unsaturated, contains three methoxyl groups, is hydrolyzed to a @-ketonic ester, and yields *m*-nitrobenzaldehyde when ozonized. It is, therefore, an open-chained compound that has a methoxyl group in the @-position.



I II III

When the same cyclopropane derivative is allowed to react in the cold with a methyl alcoholic solution of sodium dimethyl malonate—a relatively strong base—it is rapidly and quantitatively converted into the sodium salt of an unsaturated compound which contains two malonic ester residues and likewise gives m-nitrobenzaldehyde when ozonized

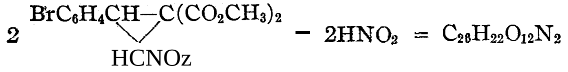


$$\underset{\displaystyle \text{HCNO}_2}{\text{NO}_2\text{C}_6\text{H}_4\text{CH—C(CO}_2\text{CH}_3)_2} \longrightarrow \text{NO}_2\text{C}_6\text{H}_4\text{CH=}\underset{\displaystyle \text{CH(CO}_2\text{CH}_3)_2}{\text{C}}\text{—CH(CO}_2\text{CH}_3)_2 \qquad \text{IV}$$

From these two reactions it is clear that bases open the new cyclopropane derivative between the carbon atoms numbered 1 and **3.** Since this is the same point at which they open the chain in the nitrocyclopropane derivative represented by **A** while that in C is opened between the atoms numbered 2 and **3,** it is evident also that the presence or absence of hydrogen in the 1-position does not affect the process.

By using cold concentrated sodium methylate it was possible to secure a substance which appears to be an intermediate in the process by which the ring is opened. The cyclopropane derivative dissolved readily in the cold methylate, forming a dark red solution which by suitable manipulation could be made to yield a red crystalline sodium compound that still contained nitrogen and also had additional methoxyl. While this sodium compound appeared to be an addition product, it was not possible to establish this with certainty because the substance is extremely unstable and we found no way to purify it. Its remarkable red color is not due to the m-nitro group because unsubstituted nitrocyclopropanes of the same type likewise develop this color,

When this red sodium compound was added to a cold solution of hydrogen chloride in dry methyl alcohol it formed nitrous acid, sodium chloride, a yellow, and a colorless organic compound. The yellow product is the same unsaturated methoxyl compound (II) that is formed by the action of methyl alcoholic potassium acetate on the cyclopropane derivative. The colorless product is more interesting, because its composition and molecular weight show that it is formed from two molecules of the cyclopropane in accordance with the equation



$$2\ \underset{\displaystyle \text{HCNO}_2}{\text{BrC}_6\text{H}_4\text{CH—C(CO}_2\text{CH}_3)_2} - 2\text{HNO}_2 = \text{C}_{26}\text{H}_{22}\text{O}_{12}\text{N}_2$$

The behavior of this colorless substance is peculiar. It is extremely sensitive to basic reagents. In the presence of sodium methylate it combines with two molecules of methyl alcohol and forms, quantitatively, two molecules of the yellow unsaturated methoxyl compound II. It likewise combines with sodium dimethyl malonate in the cold and forms—again quantitatively—the same unsaturated compound (III) that is obtained by the interaction of the malonate and the cyclopropane derivative. Even potassium permanganate, which does not attack the cyclopropane derivative, readily oxidizes this colorless product in the cold. All these basic reagents cleave the molecule symmetrically.

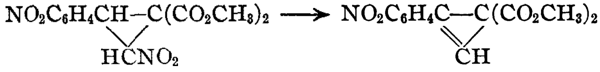
Toward acidic reagents the colorless substance is comparatively indifferent. Acids inhibit its reaction with permanganate. It does not combine with bromine. By prolonged heating with excess of bromine the two hydrogen atoms that are not located either in the phenyl or in the ester groups are replaced step by step but the carbon skeleton of the molecule remains intact. The skeleton even survives the action of concentrated sulfuric acid, which deprives the substance of two ester groups without causing cleavage. Acidic reagents in no circumstances bring about the symmetrical cleavage that invariably accompanies the action of bases.

The peculiar properties of this colorless product may be summed up in the statement that it behaves toward acidic reagents as if it were saturated and toward basic reagents as if it were an extremely sensitive unsaturated compound. Such peculiar properties must be due to an equally peculiar structure. Since the substance is cleaved symmetrically, it may be assumed that it is composed of two halves each of which has the skeleton that is present in all of its cleavage products, namely

$$NO_2C_6H_4\text{—}C\text{—}C\text{—}C(CO_2CH_3)_2$$

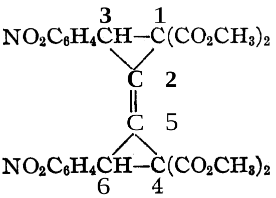
For each of these skeletons but one hydrogen atom is available, and neither of these two hydrogen atoms is sufficiently active to be detected by the Zerewitinoff method; neither is, therefore, in the a-position to the ester groups. The substance is slowly attacked by ozone but it gives neither nitrobenzaldehyde nor nitrobenzoic acid when ozonized—therefore does not, like its cleavage products, have an outlying $NO_2C_6H_4CH{=}$group.

The formation of the substance is associated with the elimination of nitrous acid from the cyclopropane derivative. As far as is known the only way in which this can occur is that represented by the equation



$$\underset{HCNO_2}{NO_2C_6H_4CH\text{—}C(CO_2CH_3)_2} \longrightarrow \underset{CH}{NO_2C_6H_4C\text{—}C(CO_2CH_3)_2}$$

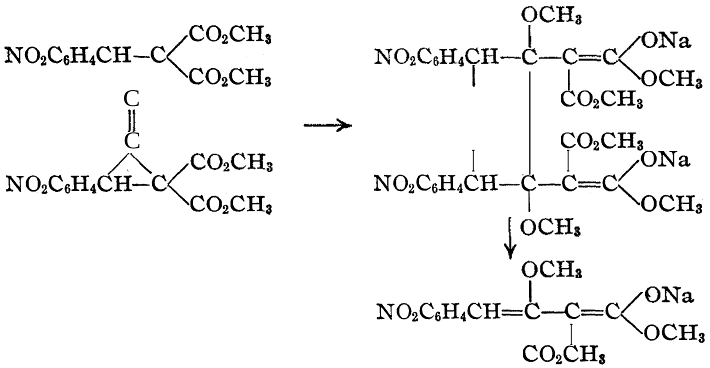
Polymerization of the resulting cyclopropene derivative in a manner that is common in ethylenic compounds would involve the usual shift of the hydrogen and of double linkages, and would lead to the formula indicated.



V

This peculiar formula, in our opinion, best expresses our present knowledge of the substance. It doubtless represents a structure with considerable internal strain, but it is not possible to construct a cyclic model that meets the requirements and has less. It manifestly accounts for the lack of active hydrogen atoms, the inability to add bromine, the sluggishness toward ozone, and the fact that ozonization does not result in nitrobenzaldehyde.

The formula also is consistent with and to a degree accounts for the cleavage of the dimer by bases. Addition of sodium methylate to a substance so constituted would, as is usual in the case of cyclopropane derivatives, lead to a 1,4-addition product, the sodium going to carbonyl, the methoxyl either to the 2- or 3-positions in the upper ring and to the corresponding positions in the lower ring. In the case of so novel a structure it would be reckless to choose between these alternatives; but if we assume that for adequate reasons the methoxyl groups seek the positions 2 and 5, then the necessary readjustments within the molecule will inevitably result in rupture of the rings between atoms 1 and 3 and between atoms 4 and 6, in cleavage between atoms 2 and 5, and in the formation of the cleavage product that is actually obtained



Experimental Part

The general scheme for securing our parent substance was the same that has been used for obtaining a number of cyclopropane derivatives—the preparation of the proper unsaturated compound, addition of nitromethane, bromination of the addition product, and elimination of hydrogen bromide from the bromo compound. In order to be able to select the most advantageous materials, we carried out these preliminary operations with a number of closely related substances.

Thus we prepared not only the methyl ester of benzalmalonic acid but also the methyl and ethyl esters of *p*-nitrobenzalmalonic and *m*-nitrobenzalmalonic acid. Except in solubility and melting point the nitrated members are, naturally, very similar to benzalmalonic esters, but we found that they combine much more readily with methyl alcohol and that the resulting addition products are sufficiently stable to survive bromination.

The unsaturated esters were prepared by the method of Knoevenagel.[1] The methyl alcohol addition products were formed by adding one equivalent of sodium methylate to methyl alcoholic solutions of the esters and, within a minute, acidifying with glacial acetic acid; the brominations

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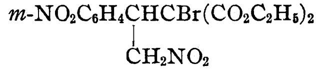
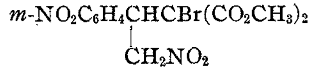
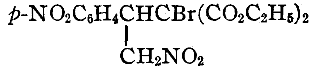
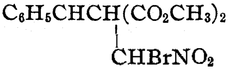
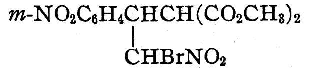
[1] Knoevenagel, *Ber.*, 31, 2593 (1898).

were carried out in dry chloroform at the ordinary temperature. All yields were good. The properties of the new substances are given in the following table.

No.	Formula	M. p., °C.	Appearance	Analyses Calcd. C	H	OCH₃	Found C	H	OCH₃
VI	$p\text{-}NO_2C_6H_4CH{=}C\text{-}(COCH_3)_2$	133-134	Leaflets	54.3	4.1		53.9	4.2	
VII	$m\text{-}NO_2C_6H_4CH{=}C\text{-}(CO_2CH_3)_2$	98-99	Small prisms	54.3	4.1		54.1	4.1	
VIII	$m\text{-}NO_2C_6H_4CH{=}C(CN)\text{-}CO_2CH_3$	135-137	Fine needles	57.0	3.3		57.3	3.4	
IX	$p\text{-}NO_2C_6H_4CH(OCH_3)CH\text{-}(CO_2CH_3)_2$	116	Leaflets	52.5	5.1	31.3	52.5	5.0	30.7
X	$m\text{-}NO_2C_6H_4\text{—}CH(OCH_3)\text{-}CH(CO_2CH_3)_2$	66	Plates	52.5	3.1	31.3	52.3	5.1	30.0
XI	$p\text{-}NO_2C_6H_4CH(OCH_3)\text{-}CBr(CO_2CH_3)_2$	133	Diamond-shaped	41.5	3.8	24.7	40.7	3.8	24.9
XII	$m\text{-}NO_2C_6H_4CH(OCH_3)\text{-}CBr(CO_2CH_3)_2$	78-80	Plates	41.5	3.8	24.7	40.9	3.7	22.4

The Nitromethane Addition Products.—The method used for adding nitromethane to the unsaturated esters was essentially that given by Kohler and Engelbrecht.[2] For preparing the a-bromo compounds the addition products were treated with bromine in dry chloroform with the help of sunlight to start the reaction when this was necessary, and the bromo compounds were isolated by removing excess bromine and solvent under diminished pressure at the ordinary temperature. For bromination in the y-position a solution of the addition product in sodium methylate was added to a solution of bromine in dry methyl alcohol. The mixture was evaporated to crystallization under diminished pressure, then diluted with water.

No.	Formula	M. p., °C.	Form	Analysis	Calcd.	Pound
XIII	 $m\text{-}NO_2C_6H_4\underset{\displaystyle CH_2NO_2}{\underset{\vert}{C}}HCBr(CO_2C_2H_5)_2$	85.5	Small rhombs	C	41.6	41.3
				H	3.9	4.1
XIV	 $m\text{-}NO_2C_6H_4\underset{\displaystyle CH_2NO_2}{\underset{\vert}{C}}HCBr(CO_2CH_3)_2$	123	Needles or cubes	C	38.5	39.1
				H	3.2	3.4
XV	 $p\text{-}NO_2C_6H_4\underset{\displaystyle CH_2NO_2}{\underset{\vert}{C}}HCBr(CO_2C_2H_5)_2$	88	Needles	C	41.6	41.6
				H	3.9	4.1
XVIa	 $C_6H_5CH\underset{\displaystyle CHBrNO_2}{\underset{\vert}{C}}H(CO_2CH_3)_2$	81.5–83	Cubes	C	43.3	43.4
				H	3.9	4.0
XVIb	Isomer	107–109	Needles	C	43.3	43.7
				H	3.9	4.1
XVII	 $m\text{-}NO_2C_6H_4\underset{\displaystyle CHBrNO_2}{\underset{\vert}{C}}HCH(CO_2CH_3)_2$	147–148	Prisms	C	38.5	38.7
				H	3.2	3.3

The Cyclopropane Derivative.—Of all the bromine compounds tabulated, the last (XVII) alone gave a satisfactory yield of a cyclopropane.

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[2] Kohler and Engelbrecht, THIS JOURNAL, 41, 764 (1919).

Fortunately this gave a single substance in almost calculated quantity. The procedure was as follows.

Dimethyl 2-(3-Nitrophenyl)-3-nitrocyclopropane Dicarboxylate, I.—Equal weights of the γ-bromo compound XII and potassium acetate were added to sufficient dry methyl alcohol to dissolve all of the acetate at the boiling point. The suspension was boiled until all of the bromo compound had dissolved, then diluted with enough water to dissolve the precipitated potassium bromide. From the resulting clear light yellow solution, the cyclopropane crystallized in almost the theoretical quantity. It was purified by recrystallization from methyl alcohol.

Anal. Calcd. for $C_{13}H_{12}O_8N_2$: M, 324; C, 48.1; H, 3.7. Found: M, 322; C, 48.1; H, 3.8.

The substance is moderately soluble in most organic solvents. It crystallizes in small hexagonal plates and melts at 122–123.5°. It does not reduce a solution of potassium pennanganate in acetone.

The same substance was obtained in a similar manner from the α-bromo compound IX. Since it is much easier to prepare this bromo compound than its isomer XVI, many efforts were made to find a satisfactory method for converting it into the cyclopropane derivative, but the yield was in all cases very small.

Reaction between the Cyclopropane Derivatives and Basic Reagents.—The cyclopropane derivative, like all the other nitrocyclopropanes, is very sensitive to bases. We studied the action of methyl alcoholic potassium acetate, aqueous alkalies, dilute and concentrated sodium methylate and the sodium derivative of dimethyl malonate. All of these reagents dissolve the substance and form brilliant red solutions, but the last alone forms a single product which is formed quantitatively and is readily isolated.

Reaction with Sodium **Dimethylmalonate,** Methyl **Benzalpropanetetracarboxylate.**—A solution of 0.8 g. of sodium in 35 cc. of dry methyl alcohol containing 7 g. of dimethyl malonate was cooled in ice water. To this solution was added 5 g. of the cyclopropane derivative. It dissolved promptly, forming a deep red solution which was boiled for a few minutes, then cooled again to 0° and poured into cold dilute hydrochloric acid. The pale yellow oil that precipitated soon solidified. By recrystallization from methyl alcohol the solid was obtained as small colorless prisms melting at 92–94°.

Anal. Calcd. for $C_{18}H_{19}O_{10}N$: C, 52.8; H, 4.6. Found: C, 52.9; H, 4.8.

The substance is very soluble in ether and boiling methyl alcohol. It neither combines with bromine nor reduces permanganate in acetone.

Ozonization.—A current of ozonized oxygen was passed through a solution of 1 g. of the substance in ethyl bromide. At the outset the absorption of the ozone was complete. After an hour, the solution was shaken with ice water and then freed from solvent in a current of air. It left an oil. This was dissolved in methyl alcohol and treated with semicarbazide. The methyl alcoholic solution soon began to deposit a crystalline semicarbazone which melted at 233–236°. The melting point remained the same when the substance was mixed with the semicarbazone of m-nitrobenzaldehyde.

Methyl Alcoholic Potassium Acetate.—A solution of 1 g. of the cyclopropane derivative and 3 g. of potassium acetate in 25 cc. of methyl alcohol was boiled for fifteen minutes, during which it turned to a bright red color. On concentrating and cooling, it deposited **0.4** g. of unchanged cyclopropane derivative. The mother liquors yielded. in addition to a small quantity of discolored oil, **0.3** g. of a substance that crystallized in yellow needles and melted at 104–105°. The same substance was obtained in larger amounts by the action of sodium methylate.

Aqueous Alkalies **and** Sodium Methylate.—The cyclopropane derivative is soluble in aqueous alkalies and in dilute sodium methylate but it is not possible to get solid products by acidifying the resulting red solutions. Solid products were finally obtained in the following manner. A solution of **10** g. of sodium in the smallest possible quantity of methyl alcohol was cooled in a freezing mixture to −5°. To this cooled solution was added, with constant shaking, **10** g. of the substance in the form of minute crystals or a fine powder. The solution at once became yellow and soon turned red. In order to hasten solution, the flask was removed from the freezing mixture and shaken until solution was complete and crystallization started. It was then returned to the freezing mixture to complete the crystallization.

The red crystalline product was collected on a suction filter, drained as completely as possible and finally washed thoroughly with anhydrous ether. Various preparations were analyzed but the results have no significance because no two preparations gave the same values. It is variable in composition, too sensitive for recrystallization, and it deteriorates at the ordinary temperature. It dissolves in water to a strongly alkaline red solution containing sodium nitrite. The yield was, uniformly, **7–7.5** g. from **10** g. of the cyclopropane derivative.

Action of Acids on the Red Sodium Compound.—When the sodium compound is **acidified** in the usual manner it yields only oily products. To get solids it is necessary to add the sodium compound to the acid. The best procedure was found to be as follows. The freshly prepared red material was ground and added gradually to an ice cold solution of hydrogen chloride gas in **dry** methyl **alcohol**. The red color disappeared and salt was precipitated. After dilution with water the solution was extracted with ether. The ethereal extract on evaporation deposited two products—one yellow and the other colorless. The mixture was separated by crystallization from a mixture of ether and petroleum ether. The relative amounts of these products varied with different samples of the red product, but the total yield was usually **4.5** g. from **7.5** g. of the red compound.

Dimethyl β-Methoxy-γ,β-nitrophenyl Vinyl Malonate, **(II)**.—The yellow product, obtained as described in the preceding paragraph, is identical with the substance that was obtained by the action of methyl alcoholic potassium acetate on the cyclopropane derivative. It crystallizes from methyl alcohol in plates and from ether–petroleum ether in thin needles which melt at 104–105°.

Anal. Calcd. for $C_{14}H_{15}O_7N$: C, **54.4;** H, **4.9;** OCH_3, **30.1; M, 309.** Found: C, **54.2;** H, **5.0;** OCH_3, 30.1; M, 301.

Ozonization.—A current of ozonized oxygen was passed through a solution of **0.45** g. of the yellow unsaturated compound in ethyl bromide for fifty minutes, after which the solvent was removed under diminished pressure and the residue shaken with ice water. The resulting colorless oil, when boiled with methyl alcoholic semicarbazide hydrochloride, formed the semicarbazone of m-nitrobenzaldehyde.

Hydrolysis to m-Nitrophenacyl **Dimethyl Malonate.—A** solution of **2** g. of the yellow unsaturated compound in aqueous methyl alcohol containing a little hydrochloric acid was boiled for an hour and a half, during which the color disappeared. The solution was then diluted with water and extracted with ether. After washing with sodium bicarbonate, the ethereal solution was shaken with saturated aqueous copper acetate, which precipitated a gray-green crystalline solid. The solid was recrystallized from benzene, from which it separated in fine needles melting, with decomposition, at 195–200°.

Anal. Calcd. for $(C_{13}H_{12}O_7N_2)Cu$: C, 48.0; H, 3.7; Cu, 9.8. Found: C, 47.8; H, 3.7; Cu, 9.6.

The free ketonic ester was obtained by shaking a suspension of the copper derivative in ether and methyl alcohol and with a little dilute aqueous hydrochloric acid. After several recrystallizations from ether–petroleum ether it was obtained in the form of fine needles melting at 64–66°.

Anal. Calcd. for $C_{13}H_{13}O_7N$: C, 52.9; H, 4.4. Found: C, 53.5; H, 4.8.

Reaction with **Semicarbazide.**—When the ketonic ester is allowed to react with semicarbazide in the usual manner, it gradually deposits a crystalline solid which melts at 177–179°. This is, doubtless, a cyclic compound because its composition corresponds to that of a substance formed from the semicarbazone by loss of water.

Anal. Calcd. for $C_{14}H_{14}O_6N_4$: C, 50.9; H, 4.2. Found: C, 50.8; H, 4.5.

The **Dimeric** Product, **VI.**—This colorless substance always constitutes the major portion of the mixture obtained by treating the cyclopropane derivative with bases and acidifying. It crystallizes in needles and melts at 115–116°.

Anal. Calcd. for $C_{26}H_{11}O_{12}N_2$: M, 555; C, 56.3; H, 4.0; OCH_3, 22.4. Found: M, 566; C, 56.1; H, 4.2; OCH_3, 22.9.

Oxidation.—A solution of the substance in acetone reduced a solution of permanganate in the same solvent as rapidly as it was added. The principal oxidation product was m-nitrobenzoic acid, which was identified by comparison with a sample on hand. In addition to this there was formed a minute quantity of a neutral oil which could not be identified. A current of ozonized oxygen containing about 6% ozone was passed through a solution of the substance in pure dry ethyl bromide. Ozone appeared in the effluent gas from the outset, and no ozonide appeared in the liquid. After one and one-half hours the solvent was removed and the residue decomposed in the usual manner; it yielded only oily neutral products. When these oils were collected in methyl alcohol and treated with semicarbazide they formed a minute quantity of the semicarbazone of m-nitrobenzaldehyde. Repeated ozonizations in chloroform and in glacial acetic acid likewise gave only oily products.

Bromination.—The colorless substance does not combine with bromine. A chloroform solution containing one equivalent of bromine was boiled for two hours, then allowed to stand overnight. After removing solvent and excess of bromine there remained a colorless oil that soon solidified. The solid crystallized from a mixture of methyl alcohol and benzene in fine silky needles melting at 154–155°.

Anal. Calcd. for $C_{26}H_{21}O_{11}N_2Br$: C, 49.6; H, 3.5. Found: C, 49.6; H, 3.6.

This substance is evidently a monobromo derivative of the cyclic compound. When it was boiled with excess of bromine in chloroform it very slowly lost hydrogen bromide but even after twenty hours some unchanged substance was recovered along with oily bromine compounds.

Action of Concentrated Sulfuric Acid.—Five grams of the finely powdered substance was added to 50 cc. of pure concentrated sulfuric acid. The substance dissolved to a clear colorless solution which gradually became yellow, acquired the odor of sulfur dioxide and evolved a small quantity of gas. After fifteen minutes the solution was stirred into chipped ice. A light yellow solid separated. It was collected on a filter, thoroughly washed with water and dissolved in ether. The dried ethereal solution on evaporation deposited a mixture of two substances, which was separated by laborious fractional crystallization from mixtures of chloroform, benzene and petroleum ether.

One of the substances crystallized from benzene and petroleum ether or chloroform and petroleum ether in colorless plates that melt with effervescence at 122°. The effervescence is due to water of crystallization. The same substance crystallizes from methyl alcohol in colorless needles which melt at 156–157°, which is also the melting point of the dehydrated form.

One of the substances has a tendency to extract amorphous coloring matter from the solution and separate in orange colored crystals, but if its solution in benzene is shaken with fuller's earth and then diluted with petroleum ether, it separates in stout canary-yellow needles that soften at 135° and melt at 140'.

Anal. Calcd. for $C_{22}H_{18}O_8N_2$: M, 438; C, 60.3; H, 4.1; OCH_3, 14.0. Found: M, 458; C, 60.0; H, 4.0; OCH_3, 12.7.

The substance is readily soluble in benzene and in chloroform, sparingly soluble in ether and in methyl alcohol. It reduces permanganate rapidly but m-nitrobenzoic acid was the only product that could be isolated.

The second substance that was formed by the action of concentrated sulfuric acid separated from benzene and petroleum ether in colorless plates which melted with effervescence at 122". The effervescence is due to loss of water, which can be removed by heating it at 100° in a Fischer pistol. Since the molecular weight of the hydrated form in freezing benzene is only about half that of the anhydrous form, the loss is evidently due to water of crystallization. The anhydrous form crystallizes from methyl alcohol in colorless needles and melts at 157°.

Anal. Calcd. for $C_{24}H_{20}O_{11}N_2.H_2O$: H_2O, 3.4. Found: H_2O, 3.0.

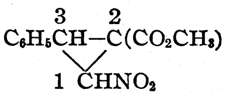
Anal. Calcd. for $C_{24}H_{20}O_{11}N_2$: M, 512; C, 56.2; H, 3.9; OCH_3, 12.1. Found: M, 528; C, 55.5; H, 4.1; OCH_3, 14.3.

This substance seems to be some sort of an anhydride of a dibasic acid formed by hydrolysis and reduction of the dimer. It is not an acid and it differs from all the other complex products in that it does not reduce permanganate in acetone.

Reaction with Basic Reagents, Sodium Methylate and Sodium Diethyl Malonate.—A quarter of a gram of the "dimer" was dissolved in an excess of dilute sodium methylate at the ordinary temperature and the resulting red solution acidified with dilute acid. It deposited the unsaturated yellow methoxyl compound in the calculated quantity. The reaction with sodium dimethyl malonate was carried out in the same manner. The dimer behaved exactly like the cyclopropane derivative and gave an excellent yield of the same m-nitrobenzal derivative.

Summary

1. The action of bases on the cyclopropane derivative



$$\overset{3}{C_6H_5CH}-\overset{2}{C}(CO_2CH_3) \quad \underset{1}{CHNO_2}$$

results in ring cleavage between the carbon atoms in Positions 2 and 3.

2. By operating in a very particular manner it is possible to isolate a dimeric product which has a peculiar structure and which appears to be an intermediate between the cyclopropane derivativd and the open-chained ethylenic cleavage products.

Converse Memorial Laboratory
Cambridge, Massachusetts

NEW BOOKS

August **Kekulé.** By Richard Anschütz. Vol. I. Leben und Wirken. (Life and Work.) Vol. II. **Abhandlungen,** Berichte, **Kritiken, Artikel, Reden.** (Communications, Reports, Criticisms, Articles, Addresses.) Verlag Chemie, G. m. b. H., Berlin W 10, Germany, 1929. Vol. I. xxiv + 708 pp. 120 illustrations. Vol. II. xvi + 960 pp. Illustrated. 17.5 × 25 cm. Price, M. 120.

Thirty-three years ago, Richard Anschutz at the request of Emil Fischer began the preparation of what was at first intended to be a "Nachruf" of KekulC for the Berichte of the German Chemical Society. Through the years, this has become the masterly biography which is now before us.

No one could have been better qualified for this task than was Anschütz. He came to Bonn in 1875, at the height of KekulC's intellectual and scientific activities, to be Kekulk's lecture assistant. He came from Darmstadt, KekulC's home city, and this biography was completed in that city. He remained with Kekulé as assistant, pupil, associate and friend until KekulC's death in 1896.

The biography is divided into two volumes. The first is devoted to the life and work of Kekulk, while the second contains a complete compilation of his publications, some one hundred and twenty-five in number, and of his addresses. The author has not made the mistake of writing one account of KekulC's life and another separate discussion of his scientific contributions. KekulC's scientific activities, like those of every great scientist, were the dominating events of his life, and Anschütz has wisely and skilfully woven them into the fabric of his biography.

And Kekulé's life offers a splendid opportunity for a biographer! Kekulk was a student of Liebig at Giessen, of Dumas, Wurtz and Gerhardt in Paris, an assistant of von Planta in Switzerland and of Stenhouse in London. He was Privatdocent at Heidelberg in Bunsen's time, Professor at Ghent at Stas' solicitation and finally Professor at Bonn. This wide experience in the leading countries of Europe brought KekulC into contact with practically all the great figures in the chemical science of the second half of the nineteenth century. Again, KekulC was a protagonist both experimentally and theoretically in the most important developments of chemistry during his period. Anschütz has taken full advantage of these exceptional opportunities, and the biography is not only an excellent account of Kekulé's life and achievements but an illuminating study of the development of chemistry during these important years.

"The biographer's task was further lightened by the fact that KekulC was an inveterate collector; he collected butterflies, plants, minerals, chemical preparations and photographs of his teachers, friends, fellow-workers and pupils. He preserved letters written to him by his colleagues, to the number of several thousand. These have added greatly to the interest of the biography. Many of the photographs are of particular interest because they represent the contemporaneous youthful appearance of their subjects, as contrasted with the more usual photographs taken in maturer years.

In addition to KekulC's already published contributions, this biography contains new material of much historical interest, for instance, the "Cassirte Kapitel zur Geschichte der Benzol Theorie und der Valenz Theorie," which Kekulé prepared in reply to the violent attacks of Kolbe but which his friend Volhard dissuaded him from publishing; also an account, previously unpublished, of KekulC's lecture on the structure of pyridine, given before the German Chemical Society at the celebration of the twenty-first anniversary of the Benzol Theory.

All told, this biography is indeed an outstanding achievement. It is not merely the labor of a lifetime by a devoted friend, but it is also a critical presentation of KekulC's contributions toward the solution of the great chemical problems of his time, written by an eminently qualified scholar. Anyone interested either in the development of the theories of valence and of the structure of organic substances, or in the great figures of our science during this period, should not fail to read this excellent biography.

ARTHUR B. LAMB

Smith's College Chemistry. BY JAMES KENDALL, F.R.S., **Professor of Chemistry in the University of Edinburgh. Revised edition. The Century Co., 353 Fourth Ave., New York, 1929. xii + 759 pp. 179 figs. Illustrated. 14.5 × 22 cm. Price, $3.75.**

In this revision of what is probably the most commonly used of the Smith texts, Dr. Kendall has made many improvements. The most noticeable of these is the rearrangement of topics so as to introduce the atomic theory early in the book. At the same time, the chapter on atomic weights and crystal structure has been expanded and improved. This has enabled him to give explanations of chemical action in modern terms practically from the beginning. Early mention is also made of the ion and a simple explanation of electrolysis is given at its first mention.

While Dr. Kendall has not yet given up the old system of ionization, he has explained much more clearly the reasons for the newer view. We still suggest as in a previous review that if the subject be taken up according to the modern standpoint from the beginning, the idea of complete dissociation will be as easily grasped as the older one. It is not necessary to give to a beginner the mathematics of Debye and Hiickel any more than it is necessary to accompany a statement of the old theory with its mathematical treatment in order to make it intelligible.

The distinction between primary and secondary products of ionization is still not sharply drawn, although the inaccurate statement of the original texts has been avoided.

The book is printed on larger pages and through the introduction of new matter has been considerably expanded.

There are many new illustrations which add to the attractiveness of the book. The line drawings, however, for some reason do not appear to print as well as formerly, possibly because they have been complicated by shading.

Taken altogether the book is the best we have seen since the edition of 1916 and a decided improvement on Dr. Kendall's first revision of the Chemistry for Colleges.

P. A. BOND

A Laboratory Outline of Smith's College Chemistry. BY JAMES KENDALL, F.R.S., Professor of Chemistry in the University of Edinburgh. Revised edition. The Century Co., 353 Fourth Ave., New York, 1929. vii + 198 pp. 32 figs. 14.5 X 22 cm. Price, $1.50.

This laboratory manual, which is designed to accompany the College Chemistry and the Inorganic Chemistry by the same author, is much like its predecessors. Some additional experiments have been inserted and new questions have been added in places where closer reasoning regarding the experiment has seemed desirable. The size of the pages has been increased slightly in order that the student may be able to use the blank interleaves to a better advantage. References are to both the College and Inorganic Chemistry.

P. A. BOND

Anorganische Chemie. Ein Lehrbuch zum Weiterstudium und zum Handgebrauch. (Inorganic Chemistry; a Textbook for Advanced Study and for Reference.) BY DR. FRITZ EPHRAIM, Professor at the University of Berne. Fourth revised and enlarged edition. Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany, 1929. xii + 809 pp. 81 figs. 16.5 X 24.5 cm. Price, unbound, RM. 28; bound, RM. 30.

In spite of the relatively short time that has elapsed since the appearance of the last edition (1923) of this book, there have been noteworthy advances in our knowledge both of descriptive and of theoretical inorganic chemistry. Thus no fewer than five new elements have been discovered— Hafnium, the higher homolog of manganese, Masurium and Rhenium, Illinium the last missing rare earth metal and Protactinium. Even more striking advances have been made in our knowledge of the structure of the atom and of the relationships of the elements.

To give adequate consideration to this new material the present edition is about 10% larger than the preceding one; it has also been extensively revised, particularly in the introductory sections dealing with the structure of the atom and the periodic system of the elements, and in the later sections dealing with halogeno salts, the compounds of the metals with one another, the fourth group of the periodic system and the rare earths.

The book maintains its emphasis on the descriptive rather than the theoretical aspect of the subject. It succeeds, better than any other text of its size with which I am familiar, in presenting the innumerable discrete facts of descriptive inorganic chemistry in a correlated and easily comprehensible form. The appearance of translations of this book into English, Spanish and Italian is an evidence of the well-deserved appreciation which it enjoys.

ARTHUR B. LAMB

A Text-book of **Inorganic** Chemistry. Edited by J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C. Vol. X. The Metal-ammines. By MISS M. M. J. SUTHERLAND, D.Sc., F.I.C., Royal Technical College, Glasgow. J. B. Lippincott Company, Philadelphia, 1928. **xxvi** + 260 pp. 15.5 X *23* cm.

The ammines of cobalt and of chromium are widely known and have been described systematically, for instance in the Seventh Edition of the Gmelin-Kraut Handbook. The ammines of the other metals have not been so adequately considered.

The present volume describes the ammines of all the metals and in the order in which the metals occur in the Periodic System, thus keeping this volume in line with the others of the Series. There are also brief introductory chapters on the history and general characteristics of the metal ammines.

This volume should be useful to those concerned with these interesting substances.

ARTHUR B. LAMB

The Journal of the
American Chemical Society

VOL. 52 FEBRUARY, 1930 No. 2

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

THE PREFERENTIAL CATALYTIC OXIDATION OF CARBON MONOXIDE IN THE PRESENCE OF HYDROGEN. I THE ACTIVITY OF TWO WATER GAS CONVERSION CATALYSTS, OF COPPER OXIDE, OF MANGANESE DIOXIDE AND OF A MIXTURE OF THESE OXIDES

BY WARD E. KUENTZEL

RECEIVED MAY 16, 1929 PUBLISHED FEBRUARY 6, 1930

Present practice in the Haber–Bosch process utilizes water gas containing nitrogen, which is mixed with three to four volumes of steam and passed in contact with promoted iron oxide catalysts to yield a 3:1 hydrogen–nitrogen mixture suitable for the synthesis of ammonia after removal of the 1–2% of residual carbon monoxide and the 29–30% of carbon dioxide by scrubbing with cuprous ammonium carbonate or formate solution and water, respectively.

The practicability of a catalytic preferential oxidation process for the removal of carbon monoxide from hydrogen has long been recognized provided the concentration of the carbon monoxide does not exceed 0.5%.[1] Higher concentrations invariably led to reduction of the oxide catalysts by the hydrogen, due to difficulties in heat dissipation.

The necessity of rapid dissipation of the heat of reaction was stressed by Lamb, Scalione and Edgar,[1d] who pointed out the possibility of utilizing hopcalite[2] to oxidize preferentially 0.5% of carbon monoxide in hydrogen by adding air sufficient to give a slight excess of oxygen over that required for complete combustion of the carbon monoxide, saturating the mixture with water vapor at 40° and passing it over hopcalite contained in a small

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[1] (a) Harger and Terrey, Brit. Patent 127,609 (1917); U. S. Patent 1,366,176, Jan. 18, 1921; (b) Rideal and Taylor, British Patent 129,743 (1918); U. S. Patent 1,375,932, April 26, 1921; (c) Rideal, J. Chem. *Soc.*, 115, 993 (1919); (d) Lamb, Scalione and Edgar, THIS JOURNAL, 44, 738 (1922); (e) Frazer, Lamb and Merrill, U. S. Patent 1,418,246, May 30, 1922.

[2] Mixtures of finely divided manganese dioxide with various metallic oxides, such as copper, cobalt, silver, etc., have been termed hopcalite. (a) Lamb, Bray and Frazer, J. *Ind. Eng. Chem.*, 12, 213 (1920); (b) Frazer and Scalione, U. S. Patent 1,345,323, June 29, 1920.

bore copper tube immersed in a liquid-bath. These investigators, as well as others,[3] also showed the importance of water vapor, which seemingly "poisons" the hopcalite toward the oxidation of both hydrogen and carbon monoxide, but more especially toward that of the former. Furthermore, in accord with the results of Lamb and Vail, the water vapor concentration of the gas phase may be greatly increased since their results indicated that the activity of hopcalite was dependent, not upon the water vapor concentration of the gas phase, but upon the actual water content of the catalyzer material and at the same time practically independent of the temperature. It should be possible, therefore, to utilize a large excess of steam in the gas phase at somewhat elevated temperatures in the preferential oxidation process over hopcalite. The use of three or four volumes of steam per volume of gas would then furnish a means of preventing local overheating of the catalyst granules by diluting the reaction mixture and of dissipating the heat of reaction by virtue of the heat capacity of the large volume of steam. The object of the present investigation was to determine experimentally whether under these conditions the higher concentrations of 1–2% or more of carbon monoxide could be efficiently oxidized.

Part I of this paper will refer to preliminary trials of a number of possible catalysts including two catalysts of the water gas conversion type, doubly promoted iron oxide and singly promoted cobalt oxide; two single oxides, copper oxide and manganese dioxide; and two hopcalite mixtures, a 2-component and a 5-component catalyst. Part II will include the more exhaustive tests with a commercially prepared hopcalite of the 2-component type.

Apparatus, Materials and Procedure

The essential features of the apparatus are shown in Fig. 1. By means of the three flowmeters, Q, R and S, mixtures of carbon dioxide and air with a carbon monoxide–hydrogen–nitrogen mixture could be continuously prepared. The gases passed through the indented tube U, which served as a mixing chamber. A continuous flow of steam, generated electrically in the boiler X, met the gas stream at the point G. The mixture of steam and gas could then be passed either through the catalyst tube Y, or through a by-pass depending upon the position of the two stopcocks H and I. The top of the steam generator and the tubes connecting this apparatus with the catalyst tube were heated to above 100° to prevent the condensation of steam. After passage through the condenser J, where the excess steam was condensed and removed through the trap K, the gases could be passed out either (1) to waste through the downward outlet cock L, or *(2)* partly through the capillary tube M to waste, and partly through the caustic potash scrubber N and soda-lime tube O, for complete removal of carbon dioxide, to the flowmeter P and thence to the carbon monoxide analyzer. The capillary tube M was so proportioned as to cause the proper flow of gas through the analyzer.

Catalysts.—The copper oxide, manganese dioxide and 5-component hopcalite were well preserved samples which had been prepared by the

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[3] Lamb and Vail, THIS JOURNAL, **47,123 (1925).**

Chemical Warfare Service investigators in 1918 during the development of hopcalite. The two water gas catalysts were prepared several years before this investigation by Mr. M. C. Molstad, at this Laboratory. The method of preparation, source and approximate composition of the catalysts are shown in Table I.

TABLE I

CATALYSTS

Catalyst	Method of preparation	Source	Approximate composition
No. 50	Pptn.	FNRL	94 parts Fe as Fe_2O_3, 5 parts Al as Al_2O_3, 1 part K as KOH
No. R-5	Pptn.	FNRL	95 parts Co as Co_2O_3, 5 part.: Al as Al_2O_3
Copper oxide	Pptn.	CWS	100% CuO
Manganese dioxide	Electrolytic	CWS	100% MnO_2
2-Component hopcalite	Mixture of the CuO and MnO_2	...	60% MnO_2, 40% CuO
5-Component hopcalite	Pptn.	CWS	39% MnO_2, 30% CuO, 17% Co_2O_3, 8% Fe_2O_3, 6% Ag_2O

Temperature of the Catalyst.—In some of the tests the catalyst was maintained at a constant temperature by immersion of the catalyst tube in a well-stirred, manually controlled glycerine bath. The catalyst temperature as recorded in the data was taken as that of a mercury thermometer immersed in the bath liquid near the catalyst chamber. The temperature was constant to within 1 or 2°. In other tests a vapor-bath boiling at the prevailing atmospheric pressure was used. The temperature here was constant to within 0.5°. The temperature bath and control device shown in Fig. 1 were used in the work presented in Part II and have been described elsewhere.[4]

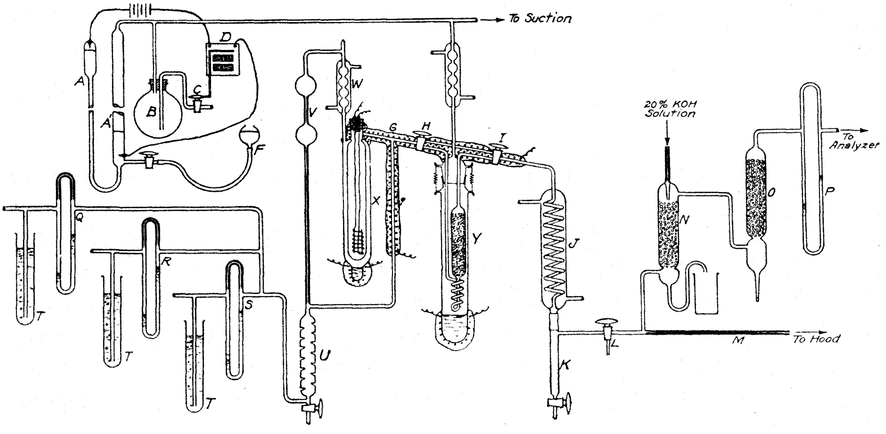

Fig. 1.—Apparatus.

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[4] Kuentzel, THIS JOURNAL, 51, 3847 (1929).

Preparation of the Gases.—The carbon monoxide was made by the interaction of formic and sulfuric acids and freed from acid and carbon dioxide by bubbling through potassium hydroxide solution. A supply of gas mixture containing 1.6% of carbon monoxide was made by compressing a 3:1 hydrogen–nitrogen mixture[5] to 135 atmospheres' pressure in a cylinder previously filled with the required amount of carbon monoxide. Oxygen or air and carbon dioxide were added to this gas mixture before it entered the catalyst chamber. The air was taken from the laboratory service lines with no purification other than a cotton–wool dust trap. The carbon dioxide was the unpurified commercial product. Tests in which continued high carbon monoxide oxidation efficiencies were obtained proved the absence of catalyst poisons from these materials.

Procedure.—Each experiment consisted in passing a 3:1 by volume steam–gas mixture at 720 dry gas space velocity over one of the catalysts at a fixed temperature and analyzing the effluent gases. Samples were taken, after condensation of the excess steam at the downward outlet stopcock I, (Fig. 1), directly into an improved Orsat type of gas analysis apparatus equipped with a long 100-cc. compensated buret and analyzed in the usual way.

In order to obtain more accurate data, the continuous carbon monoxide analyzer described by White[6] was used in the final experiments. When the continuous analyzer was operating, a constant flow of gas through this instrument provided analytical data as often as desired.

Experimental Results

Experiments with Water Gas Conversion Catalysts.—The results of experiments in which two precipitated water gas conversion catalysts, No. 50 and No. B-5, were tested as preferential oxidation catalysts indicated that these catalysts were of little or no value as selective oxidation agents. Practically identical results were obtained with gas containing no oxygen and with gas containing oxygen 100% in excess of that required for complete oxidation of the carbon monoxide present. In the case of the iron oxide catalyst, No. 50, a separate test in which the steam–gas ratio was varied from 0 to 8 resulted in the establishment of the water gas equilibrium regardless of oxygen content up to 100% in excess. When the steam content was decreased or cut off entirely in the case of the cobalt oxide catalyst, No. B-5, however, the carbon monoxide was converted to methane. These catalysts, therefore, are in the presence of an excess of steam predominantly water gas conversion catalysts. The addition of air to the final stages of a water gas converter operating at a lower temperature would have little or no effect upon the carbon monoxide content of the effluent gases.

Experiments with Copper Oxide.—The results of a few typical tests with a copper oxide catalyst are shown in Table II.

A preliminary test indicated that only about 50% of the influent carbon monoxide could be oxidized at temperatures up to 174°. From 185 to 225° the results were characterized by excessive reduction of the oxide

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[5] Prepared in a moderate scale plant similar to that described by Ernst, Reed and Edwards, *Ind. Eng. Chem.*, **17**, 775 (1925).

[6] E. C. White, THIS JOURNAL, **50**, 2148 (1928).

TABLE II

ACTIVITY OF COPPER OXIDE CATALYST

S. V. 720. Steam–gas ratio, 3:1. Influent gas compn.: CO_2, 27 5%; CO, 1.1%; O_2, 1.1%; CH_4, 0.3%; Hz, 47.6%; N_2, 22 6%

Cat. temp., °C.	Time[a]	Effluent gas				Percentage efficiency of oxidation of		Oxygen removed from cat. mg./min.
		CO, %	O_2, %	H_2, %	N_2, %	CO	H_2	
185	8 min.	0 2	0 3	462	242	822	9 3	3.2
185	23 min.	1	3	471	23.5	5 4	4 9	1.6
185	5 75 hrs	.3	3	479	23.4	724	2 7	0.4
200	3 25 hrs.	3	3	47 4	23 4	72 4	3 8	.9
200	5 6 hrs	3	.2	473	23.4	724	4 1	.9
216	5 min.	2	.3	459	238	820	8 7	3.0
216	2 5 hrs.	.3	.4	468	23.6	726	5.7	1.8
225	45 min.	.3	.2	47.1	23 6	72.7	5 5	1.3
185	1.25 hrs.	.7	.2	47.3	23.3	345	3.6	0.2

[a] The accumulated time of testing at each temperature is indicated in this column

catalyst, as shown by the last column of Table II, in which the mg. of oxygen removed from the catalyst have been tabulated. This was true especially during the first few minutes of the test at each succeeding higher temperature. High carbon monoxide and hydrogen oxidation efficiencies were usually obtained during this initial period of excessive reduction. When the amount of reduction decreased, the efficiency of carbon monoxide and hydrogen oxidation also diminished. This behavior indicated that during the first part of the test at a given temperature the catalyst was so active that both carbon monoxide and hydrogen were oxidized, not only catalytically by means of the free oxygen but also chemically at the expense of the oxygen content of the catalyzer itself. This loss of oxygen on the part of the catalyst resulted in lower activity toward both carbon monoxide and hydrogen oxidation, but more especially toward the oxidation of the latter.

Operation at the lower temperature of 185° after high temperature treatment at 225' resulted in decreased efficiencies. This was probably due to the excessive reduction occurring at the higher temperatures. Copper oxide, therefore, although catalytically active in the oxidation of carbon monoxide is partially reduced by carbon monoxide and hydrogen to such an extent that its activity is markedly impaired. Its use as a preferential oxidation catalyst for the removal of over 1% of carbon monoxide from hydrogen in the presence of carbon dioxide and a large excess of steam is not recommended.

Experiments with Manganese Dioxide.—The results obtained with a sample of electrolytic manganese dioxide are shown in Table III.

With this particular sample the carbon monoxide oxidation efficiency was markedly low at 167° and reached a value of only 91% at the high temperature of 250°. Even then it fell off to 77% after only a short time of testing. At these temperatures the catalyst was appreciably reduced, as shown by the loss of oxygen in the last column of Table III. This particular catalyst is therefore of little value as a selective oxidation agent under the conditions of steam and gas compositions here encountered.

TABLE III

ACTIVITY OF MANGANESE DIOXIDE CATALYST

S. V. 720. Steam–gas ratio, 3:1. Influent gas compn.: CO_2, 27.5%; CO, 1.1%; O_2, 1.1%; CH_4, 0.3%; H_2, 47.6%; N_2, 22.6%

Cat. temp., °C.	Time[a]	Effluent gas				Efficiency of oxidation of		Oxygen removed from cat., mg./min.
		CO, %	O_2, %	H_2, %	N_2, %	CO	H_2	
167	5 min.	0.6	1.1	47.7	23.6	45.3	4.1	2.1
190	1.5 hrs.	.3	0.9	47.2	23.4	72.4	4.1	1.9
200	15 min.	3	.8	46.9	23.3	72.5	4.3	1.9
215	3.75 hrs.	.3	.5	47.2	23.4	72.5	4.5	1.5
221	25 min.	.2	.3	47.6	23.5	81.7	3.9	0.9
230	35 min.	.3	.2	47.7	23.5	77.1	3.5	0.7
250	10 min.	.1	.2	46.6	24.2	91.1	8 6	2.8
250	1.25 hrs.	.3	.2	47.3	23.7	77.3	5.5	1.5
200	30 min.	.6	.7	47.9	23.3	49.2	2.4	0.8
220	1.75 hrs.	.3	.5	47.8	23.3	72.3	2.6	0 7
230	35 min.	.3	.3	47.8	23.4	77.8	5.0	1.3

[a] The accumulated time of testing at each temperature is indicated in this column.

Experiments with a 2-Component Hopcalite.—A 2-component hopcalite catalyst was prepared by weighing out unused portions of the two previously tested oxides in the proportions of 60% of manganese dioxide to 40% of copper oxide and mixing them in a finely ground wet paste. Most of the water was then filtered off, the mixture kneaded and finally pressed under hydraulic pressure of about 2000 pounds per square inch. The resulting product was dried at 50°, crushed and screened to 6–10 mesh and then finally dried at 190°. The results of tests on this material are shown in Table IV.

TABLE IV

EFFECT OF MIXING MANGANESE DIOXIDE AND COPPER OXIDE IN THE PROPORTION OF 60:40 BY WEIGHT

S.V. 720. Steam–gas ratio, 3:1. Influent gas compn : CO_2, 27.5%; CO, 1.1%; O_2, 1.1%; CH_4, 0.3%; H_2, 47.6%; N_2, 22.6%

Cat. temp., °C.	Time[a]	Effluent gas				Efficiency of oxidation of		Oxygen removed from cat., mg./min.
		CO, %	O_2, %	H_2, %	N_2, %	CO	H_2	
150	5 min.	0.1	1.3	46.3	23.9	91.0	8 2	4.4
150	9.5 hrs.	.2	0.7	48.2	23.0	81.3	0.7	0.3
163	2.5 hrs.	.1	.6	47.9	23.0	95.3	1 2	5
150	3 hrs.	.2	.6	48.5	23.3	81.5	1.1	.4
163	2 hrs.	.1	.5	48.3	23.2	90.7	1.1	.3

[a] The accumulated time of testing at each temperature is indicated in this column.

The effect of simply mixing the two constituent catalysts was very marked. Over 90% of the influent carbon monoxide was oxidized at a temperature of only 150" during the first hour of operation, and after nine and one-half hours over 81% efficiency was still obtained. At 163° an efficiency of 95% was obtained for two and one-half hours. Operation at 150° after this gave over 81% oxidation. Such efficiencies were obtained only when the temperature ranged around 185° in the case of copper oxide alone, and over 200° in the case of manganese dioxide alone. This behavior of oxide mixtures is in accord with the observations of Almquist and Bray[7] and Bray and Doss[8] who studied the so-called "mixture effect" with these oxides. The reduction of the catalyst was quite appreciable during the initial stages of the test at 150°, but became negligible with continued operation.

Effect of High Temperature and Continued Usage upon the Activity of 2-Component Hopcalite.—The same charge of hopcalite already tested at 150 and 163° was used in determining the effect of higher temperatures. The results are given in Table V.

TABLE V

EFFECT OF TEMPERATURE ON ACTIVITY OF HOPCALITE II

S.V. 720. Steam–gas ratio, 3:1. Influent gas compn.: CO_2, 27.5%; O_2, 1.1%; CO, 1.1%; H_2, 47.5%; CH_4, 0.3%; N_2, 22.5%

Temp., °C.	Time,[a] hours	Effluent CO, %	Efficiency of oxidation of CO	Temp., °C.	Time of operation at temp. noted, hours	Effluent CO, %	Efficiency of oxidation of CO
165	3	0.078	95.0	175	1.75	0.096	93.9
175	1.5	.037	97.6	185	2	..	..
165	3	.071	95.5	190	0.5	.069	95.6
175	0.5	.051	96.8	185	0.5	.098	93.8
175	2	.050	96.8	175	0 5	.138	91.2
190	1	.021	98.7	220	1.25	.149	90.5
190	2.75	.023	98.6	220	2	.157	90.0
190	4	.050	96.8	175	0 5	.406	73.8
165	0.5	.17	89.2				

[a] The accumulated time of testing at each temperature is indicated in this column.

A study of these results, obtained with the continuous analyzer, shows that in the range 165 to 190° efficiencies of over 95% may readily be attained, but the high temperature of 220" had a marked deteriorating effect upon the activity of the catalyst. The oxides composing the catalyst were no doubt considerably reduced by this high temperature treatment.

A test was next made in which a fresh charge was maintained constantly at 175° during the passage of gas–steam mixture over it. The test was intermittent in that the catalyst was allowed to cool down to room tem-

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[7] Almquist and Bray, THIS JOURNAL, 45, 2305 (1923).

[8] Bray and Doss, *ibid.*, 48,2060 (1926).

perature overnight, but otherwise conditions were constant throughout the entire run of thirty-seven hours. An initial efficiency of nearly 99% decreased during the first fourteen hours to 96% and remained constant at this value thereafter.

Experiments with a 5-Component Hopcalite.—A few preliminary experiments were made at the beginning of this investigation with a 5-component hopcalite. At the temperature of 218° the catalyst charge was completely reduced with incandescence when the steam–gas mixture containing 1.6% carbon monoxide in 3:1 hydrogen–nitrogen mixture to which 1.6% oxygen had been added was passed over it at the high space velocity of 6000. Further tests at 720 space velocity upon fresh charges of this catalyst with 28% carbon dioxide added to the influent gases yielded practically complete oxidation of carbon monoxide initially at temperatures ranging from 162 to 200°, but only about 50% efficiency upon continued testing. No attempt was made to determine the cause or causes of its failure. It is of interest, however, to indicate that under conditions at which the 2-component catalyst gave excellent results, the 5-component catalyst was decidedly inferior.

The author wishes to express his deep appreciation to Dr. J. A. Almquist, at whose suggestion this problem was undertaken, for his kind advice and encouragement.

Summary

A study has been made of the preferential oxidation of carbon monoxide by oxygen in the presence of hydrogen and carbon dioxide and a large excess of steam in contact with the catalysts (a) promoted iron oxide, (b) promoted cobalt oxide, (c) copper oxide, (d) manganese dioxide, (e) a 5-component hopcalite and (f) a 2-component hopcalite.

Only the last named catalyst showed any promise as a preferential oxidation agent under these conditions. An efficiency of over 96% was obtained with it for a period of thirty-seven hours. The promoted iron oxide and cobalt oxide catalysts were predominantly water gas conversion catalysts and the presence of oxygen in the gas mixture apparently had no effect upon the final result, which was governed entirely by the water gas reaction, $CO + H_2O \rightleftharpoons CO_2 + H_2$. The copper oxide, the manganese dioxide and the 5-component hopcalite, although catalytically active in the preferential oxidation of carbon monoxide, suffered serious reduction with consequent loss in activity.

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THE PREFERENTIAL CATALYTIC OXIDATION OF CARBON MONOXIDE IN THE PRESENCE OF HYDROGEN. II. THE ACTIVITY OF 2-COMPONENT HOPCALITES

BY WARD E. KUENTZEL

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Introduction

Preliminary experiments[1] have shown the possibility of effectively removing the 1–2% of carbon monoxide present in converted water gas of the Haber–Bosch process by preferential catalytic oxidation over hopcalite consisting of 60% MnO_2 and 40% CuO. The present paper presents the results of an extended investigation of various factors influencing the activities of an essentially 2-component commercial hopcalite and of a 2-component laboratory scale preparation for the catalytic oxidation of carbon monoxide.

Apparatus, Materials and Procedure

The apparatus and methods, in general, were those described in Part I.[1] The catalyst was maintained at a constant temperature by means of a vapor-bath with a liquid boiling either at the prevailing atmospheric pressure or under automatically controlled reduced pressure as described elsewhere.[2] The flow of gas through the friction tube flowmeters was automatically controlled to give a constant ratio of air to gas by means of an improved modification of the device described by Oberfell and Mase.[3]

Preparation of the Gases.—Practically all of the experiments were made with actual converted water gas prepared in a moderate scale Haber–Bosch plant at this Laboratory. This consisted in the preparation of water gas from coke and steam, the "conversion" by means of steam of most of the 30% or more of carbon monoxide to carbon dioxide in contact with promoted iron oxide catalyst, the condensation of the excess steam and compression of the resulting "converted water gas" into high pressure cylinders. Air was added in the selective oxidation experiments by means of a flowmeter after expansion of the gas to atmospheric pressure.

In a few experiments pure gases rather than "converted water gas" were used. These gases were prepared as described in Part I.

Catalysts.—Two catalysts were used in the present experiments, a 6–14 mesh essentially 2-component commercial hopcalite (designated "MSA hopcalite" throughout this paper) and a 10–16 mesh 2-component hopcalite prepared at the American University Experiment Station in

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[1] W. E. Kuentzel, THIS JOURNAL, 52,437 (1030).

[2] W. E. Kuentzel, *ibid.*, 51,3347 (1929).

[3] G. G. Oberfell and R. P. Mase, *J. Ind. Eng. Chem.*, 11,294 (1819).

1918 by the Chemical Warfare Service (designated "CWS hopcalite") and preserved in a sealed jar since that time. It is highly probable that this latter catalyst and that used in preferential combustion experiments by Lamb, Scalione and Edgar[4] are identical. The compositions of these catalysts are tabulated in Table I.[5]

TABLE I

COMPOSITION OF MSA AND CWS HOPCALITES ON BASIS OF COMPLETELY DRIED MATERIAL

	Percentages												
	CuO	MnO_2	MnO	MgO	Fe_2O_3	K_2O	Na_2O	H_2O	CO_2	SO_3	SiO_2	Avail. O_2, %	Total %
MSA	12.9	77.5	5.4	1.5	1.0	1.6	...	17.8	0.1	2.0	...	15.7	102.0
CWS	45.0	42.1	3.0	1.0	2.3	0.3	0.8	10.6	4.0	0.1	0.6	12.5	99.2

Methods of Analysis.—The efficiency of carbon monoxide oxidation was determined by following the effluent carbon monoxide content with a continuous conductivity analyzer.[6] In the later experiments a shunted Leeds and Northrup recording potentiometer recorded the conductivity continuously. With these devices the carbon monoxide content of the gases could be determined accurately to 0.002%.

When a complete analysis of the gaseous mixture was required an improved exact gas analysis apparatus was used.[7]

The loss of oxygen from the oxide catalysts was obtained by determining the "available oxygen" before and after the run. The "available oxygen" was determined in the manner described by Almquist and Bray[8] except that nitrogen was used as a flushing gas instead of carbon dioxide.

Conditions of Operation.—Certain conditions of operation were chosen as standard, such as a dry gas space velocity of 1000 with 10 cc. apparent volume of catalyst; a 3:1 volume mixture of steam and gas; and an oxygen concentration approximately equal to that of the carbon monoxide. Preliminary tests with MSA hopcalite in which the effect of slight variations in these operating conditions were determined indicated that variations in space velocity of 760 to 1500 resulted only in slightly lower efficiencies at the higher space velocity with no appreciable effect on the subsequent activity at the lower space velocities. Variations in oxygen content ranging from 100 to 145% in excess of that required for complete combustion of the carbon monoxide had only a slight effect, the higher concentration always yielding only a slightly higher efficiency. Although a change in the quantity of admixed steam from 3:1 to 4:1 by volume resulted in efficiencies lower than those obtained with the standard

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[4] A. B. Lamb, C. C. Scalione and G. Edgar, THIS JOURNAL, 44, 738 (1922).

[5] The writer is indebted to Miss K. S. Love and Miss E. Z. Kibbe for analyses of the catalytic material other than water and available oxygen.

[6] E. C. White, THIS JOURNAL, 50, 2148 (1928).

[7] W. E. Kuentzel, *ibid.*, 51, 2759 (1929).

[8] J. A. Almquist and Wm. C. Bray, ibid., 45, 2305 (1923).

mixture of 3:1, no permanent injury followed the use of the higher steam concentrations, but a definite decrease in efficiency usually resulted from treatment with steam in the volume ratio of 2:1. The flow of steam could be controlled accurately to within ±1%, which precluded the possibility of any appreciable influence of the latter condition.

Experimental Results

Influence of Temperature and Continued Usage on the Activity of MSA Hopcalite.—The results of a study of the effect of temperature and continued usage upon the activity of MSA hopcalite are shown in Fig. 1.

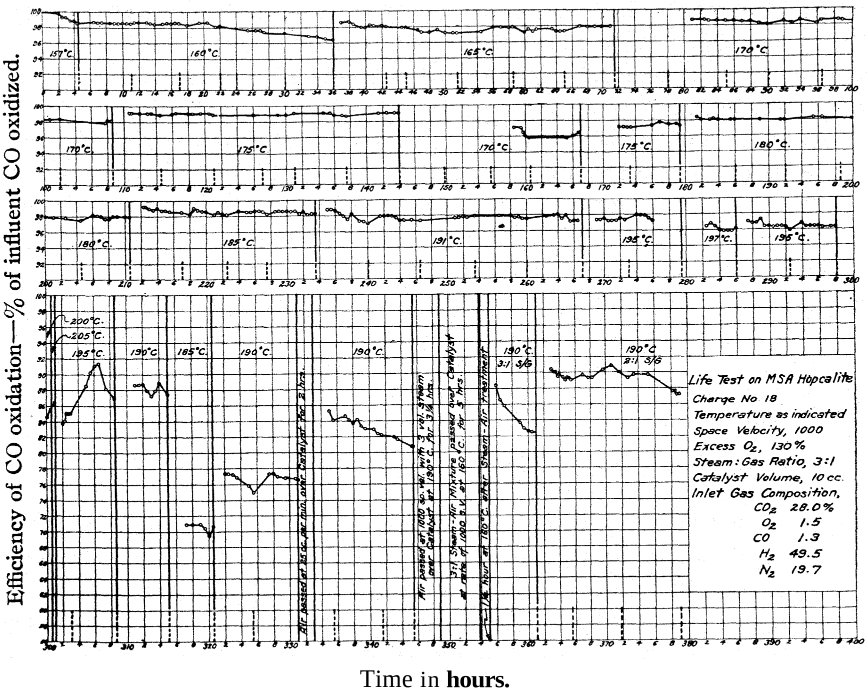


Fig. 1.

The activity was studied at progressively higher temperatures, starting at the lowest feasible temperature. These data were all obtained with a single charge of catalyst during 379 hours of actual testing. (The short vertical broken lines either along the curve or axis of abscissas indicate that the test was discontinued overnight at these points.)

A study of these data indicates that from 97 to 99% of the carbon monoxide may be oxidized in the presence of three volumes of steam to one of gas containing approximately 1.3% carbon monoxide, 1.5% oxygen, 49.5% hydrogen, 28.0% carbon dioxide and 19.7% nitrogen in the temperature range of 160 to 195°.

Attempts to restore the activity after it had been greatly decreased by high-temperature operation through the agency of re-oxidation by means of both dry air and air mixed with steam at 190 and at 160° were only partly successful. The activity at 190° was improved, but the activity at 160° was still very low after these air treatments, as shown by the single point at 56% efficiency at the 355th hour. Decreasing the quantity of steam to a 2:1 volume ratio also only slightly improved the efficiencies.

Factors Contributing to a Decrease in Efficiency of the Catalyst.—Although a high efficiency of carbon monoxide oxidation was maintained in the above tests for a considerable period of time, there is evidence that the catalyst continually decreased in activity, as indicated by the necessity of increasing the temperature in order to maintain the high efficiency, as well as by the rather rapid decrease in efficiency after high temperature operation.

Several factors which might contribute to a decrease in the efficiency of the catalyst readily suggest themselves, such as (1) reduction of the catalyst by carbon monoxide, (2) reduction of the catalyst by hydrogen, (3) loss of available oxygen through thermal dissociation of the oxides composing the catalyst, (4) insufficient dissipation of heat of reaction and (5) the possible presence of catalyst poisons. Experiments to test the part played by these various factors were accordingly carried out.

Influence of Carbon Monoxide and Hydrogen Concentration on Catalyst Reduction.—Three experiments were made at 156° in which carbon monoxide concentrations of 1.3, 0.5 and 0% were used. The results of the first two are plotted in Fig. 2, Curves 17 and 28, respectively. In the former the gas concentrations were the same as those used in the long-time test (Fig. 1), while in the latter the converted water gas entering the catalyst chamber consisted of 0.5% carbon monoxide, 0.5% oxygen, 31.2% carbon dioxide, 50.8% hydrogen and 17.0% nitrogen.

Analysis of the catalyst charges used in these two tests showed that No. 17 had lost 33.5% of the total available oxygen content of the original material during thirty-six hours of testing, whereas No. 28 lost 27.8% of its total available oxygen in twenty-five hours of testing. When due corrections are applied for the relative lengths of the runs and cognizance is taken of the fact that most of the reduction occurred in the early part of each run, it will be seen that a slightly greater loss of available oxygen occurred with the higher concentration of carbon monoxide.

The slightly greater efficiency with 1.3% carbon monoxide as compared to 0.5% may be explained by the plausible assumption that the greater heat of reaction in the former served to heat the catalyst granules to a slightly higher temperature than that existing in the latter.

The third experiment, in which the concentration of carbon monoxide was zero, was also carried out at 156°. The gas mixture prepared from pure hydrogen–nitrogen mixture, carbon dioxide and air which together with three volumes of steam entered the catalyst chamber, contained 32.0% carbon dioxide, 1.0% oxygen, 50.2% hydrogen and 16.8% nitrogen.

The activity of the catalyst was followed by determining the oxygen consumed rather than the actual decrease in hydrogen content. Samples of both influent and effluent gases were taken from time to time and analyzed for oxygen in the bulbed exact gas analysis apparatus. These analyses were then plotted against time and the quantities of oxygen entering and leaving the catalyst chamber determined by taking the areas under the smoothed curves. Upon completion of the test the loss in available oxygen was determined by analysis of the catalyst. The total hydrogen oxidized was then the sum of the hydrogen equivalents of the free and combined oxygen consumed.

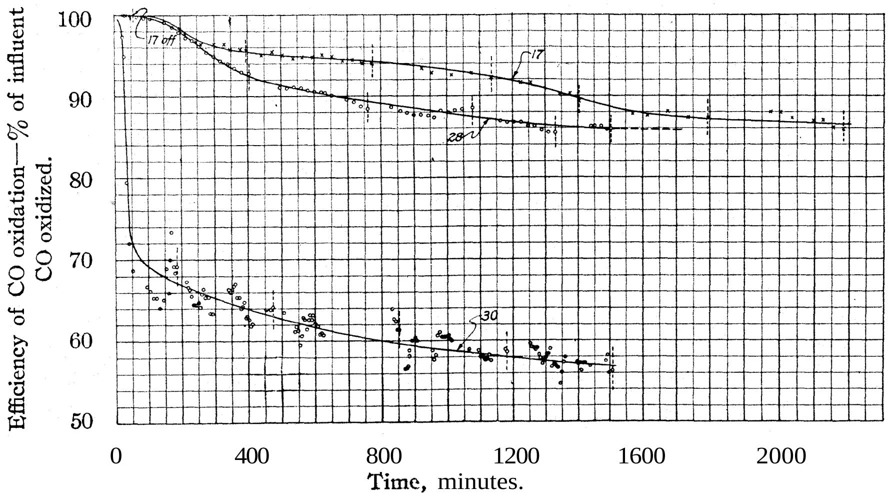


Fig. 2.—Comparison of oxidation of 0.5 and 1.3% carbon monoxide in converted water gas and effect of substituting nitrogen for steam. Curve 17—oxidation of 1.3% CO at 156°, 3:1 steam–gas mixture in glass catalyst chamber; Curve 28—oxidation of 0.5% CO at 156°, 3:1 steam–gas mixture in glass catalyst chamber; Curve 30—oxidation of 0.5% CO at 156°, 3:1 nitrogen–gas mixture in glass catalyst chamber.

A loss of 24% of the total available oxygen content of the catalyst resulted from twenty-five hours of operation, as compared to losses of 27.8 and 33.5% with hydrogen plus 0.5 and 1.3% carbon monoxide, respectively. The efficiency of hydrogen oxidation was calculated to be 1.1%.

Further evidence that the presence of hydrogen contributed to the reduction of the catalyst is shown by a comparison of the above tests utilizing carbon monoxide-free gas with tests carried out with hydrogen-free gas containing 0.5% carbon monoxide. Two tests, the results of which are plotted in Fig. 3 (Curves 31 and 32), were made at 156° with a gas mixture prepared from carbon monoxide, carbon dioxide, nitrogen and air. The mixture entering the catalyst chamber, together with three volumes of steam, contained 0.5% carbon monoxide, 0.7% oxygen, 29.1% carbon dioxide and 69.7% nitrogen. In Run 31 an accidental lowering of the temperature to 140° produced a temporary lowering of efficiency. In the duplicate test (No. 32) a very gradual decline in efficiency from 100 to 98% resulted in twenty-five hours of testing. Analysis of the catalyst charges showed losses of 18.4 and 20.3% of the total available oxygen content of the original material, respectively, compared to a loss of 24.0% with gas containing 50% hydrogen but no carbon monoxide.

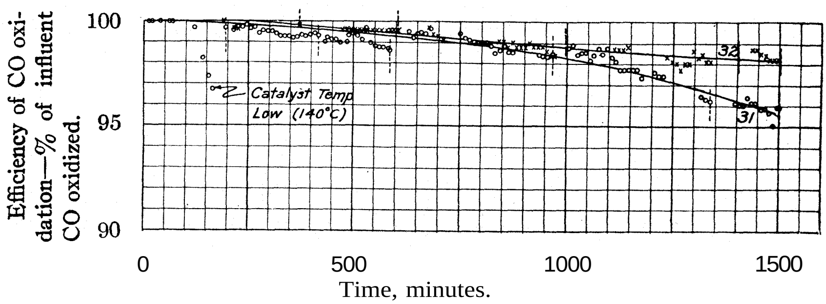


Fig. 3.—Oxidation of carbon monoxide alone. Curves 31 and 32—MSA hopcalite at 156°, 3:1 steam-gas mixture in glass catalyst chamber.

Loss of Available Oxygen by Thermal Dissociation.—In order to ascertain what fraction of the above-mentioned oxygen losses might be caused by thermal decomposition, a separate test was made. This test consisted in determining the loss in weight, other than water, of a fresh sample of the material after having been swept with dry nitrogen at 156° for 20.25 hours. This value when extrapolated to twenty-five hours, showed that the maximum loss in available oxygen would have been 8.2% due to thermal dissociation alone. The greater part of the oxygen loss in the presence of reducing gases was therefore probably due to reduction of the catalyst.

Influence of the Heat Conductivity of the Catalyst Tube on the Efficiency of the Catalyst.—Lamb, Scalione and Edgar[4] successfully oxidized 0.5% of carbon monoxide in slightly moist gas containing hydrogen over hopcalite by utilizing a copper catalyst tube to dissipate the heat of reaction. It was considered of interest to duplicate their experiments in both glass and copper catalyst chambers.

A gas mixture containing 0.5% carbon monoxide, 0.5% oxygen, 74.8% hydrogen and 24.2% nitrogen was saturated with water vapor at 40 ± 0.1° and passed over catalyst samples at a space velocity of 6000 and a temperature of 102°. The results of tests with CWS and MSA hopcalites in glass catalyst tubes are plotted in Fig. 4, Curves 35 and 36, respectively. In both instances high initial efficiencies of about 94% which rapidly decreased with time to 70 and 48%, respectively, were obtained.

An exact duplication of the conditions of Lamb, Scalione and Edgar with a copper catalyst chamber of the same general dimensions except that the copper tube preheater was somewhat shorter, gave, with new charges of the same catalysts, the results shown in Curves **37** and **38** of Fig. **4.** The CWS catalyst now gave 100% oxidation for several hours and as high as **98%** after twenty-five hours. The test was continued without interruption for sixty hours with a final efficiency of over 96%. The MSA hopcalite likewise gave a high initial oxidation efficiency, but its activity declined, rapidly at first and then more gradually to a final value of 75%. The superior activity of the CWS catalyst is quite apparent.

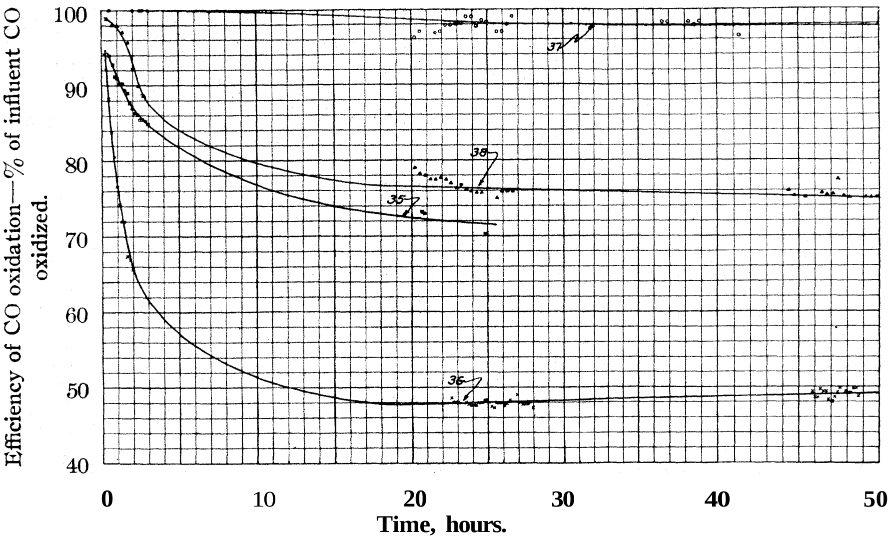


Fig. 4.—The effect of using a copper catalyst chamber. Curves 35 and 36—CWS and MSA catalysts at 102°, gas saturated with H_2O vapor at 40° in glass catalyst chamber, respectively; Curves 37 and 38—CWS and MSA catalysts at 102°, gas saturated with H_2O vapor at 40° in copper catalyst chamber, respectively.

These tests indicate, as Lamb, Scalione and Edgar have pointed out, the extreme importance of rapid and efficient dissipation of the heat of reaction. The inefficiency of the catalysts in glass as compared with copper catalyst chambers can be considered as due to the inability of the glass to conduct away rapidly the heat of reaction.

Influence of an Excess of Steam on the Efficiency of the Catalyst.—The large excess of steam used in previous tests in glass catalyst chambers probably served (1) to dissipate the reaction heat and (2) to exert a specific inhibition to oxidation of hydrogen and to reduction of the catalyst by hydrogen.[10] The necessity of using a copper catalyst chamber with slightly moist gases for dissipation of the heat of reaction and the excellent results obtained in glass with an excess of steam indicate that the steam actually served as a dissipator of heat. This was further proved by an experiment in which both steam and a copper catalyst chamber were used.

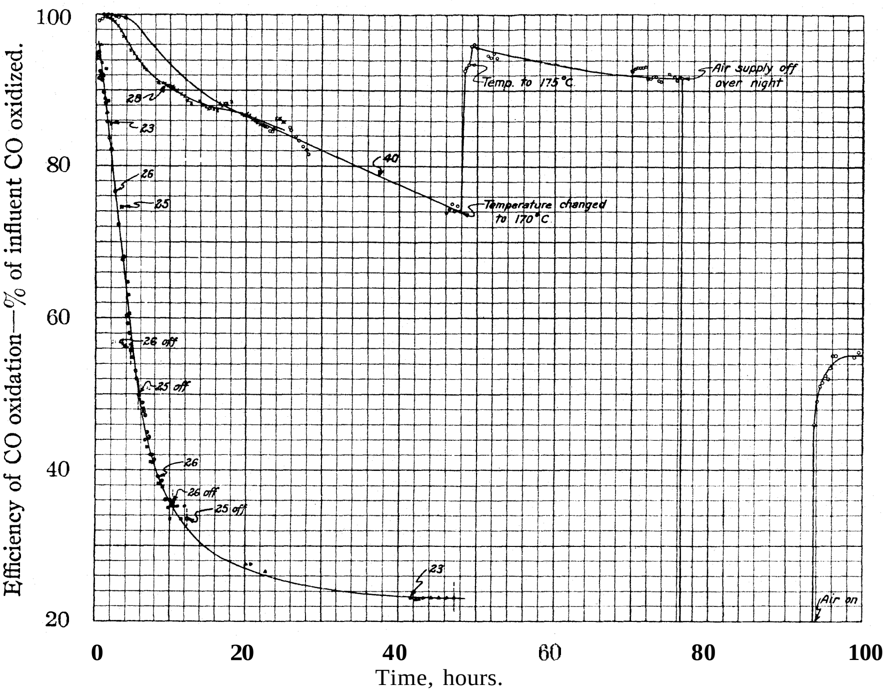


Fig. 5.—affect of steam in copper catalyst chamber and tests with purified and unpurified gases. Curve **28—MSA** hopcalite at 156°, 3:1 steam–gas mixture in glass catalyst chamber; Curves **23** and 25—tests at 130° with unpurified converted water gas; Curve 26—test at 130° with converted water gas purified by hot copper and chromic–sulfuric acid; Curve **40—MSA** hopcalite at 156°, 3:1 steam–gas mixture in copper catalyst chamber.

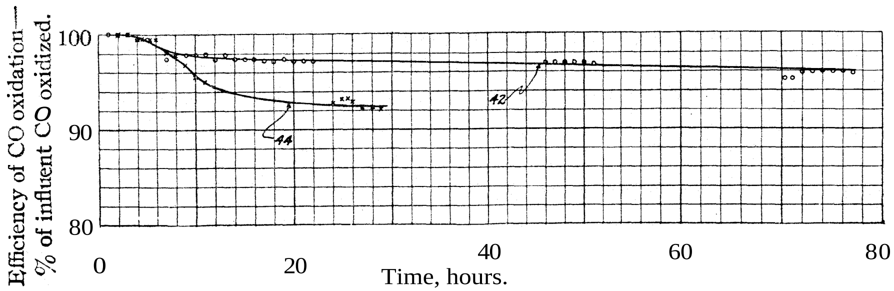
The results of a "steam-in-copper" test are plotted together with a "steam-in-glass" experiment in Curves 40 and 28, Fig. 5. Both curves show decreasing efficiencies with time; those in the glass tube fell only slightly more rapidly during the initial stages than those in the copper, but both were practically coincident after about twenty hours. It may therefore be concluded that the excess of steam eliminated overheating of the catalyst sufficiently well to make a copper catalyst tube of no added benefit.

[9] **A, B.** Lamb and W. E. **Vail, This** JOURNAL, 47,123 (1925).

[10] R. N. Pease and H. **S.** Taylor, *ibid.*, **43,2179** (1921).

Experiment No. 40 was continued for 100 hours' duration in all at temperatures up to 175°. While the catalyst was operating at an efficiency of 92% after seventy-six hours, the air supply to the catalyst was accidentally cut off overnight while gas and steam containing no oxygen passed over the catalyst for a period of about fifteen hours. When the air supply was again admitted, the efficiency was only 55%. Reduction of the catalyst occurred in the absence of oxygen. Thus it would appear that not only steam, but free oxygen as well, is essential to the prevention of the reduction of the catalyst.

The specificity of water vapor in inhibiting reduction of the catalyst was confirmed by an experiment in which nitrogen was substituted for steam. The heat capacity and consequently the heat dissipating ability of nitrogen at 156° is roughly of the same order of magnitude as that of steam, the latter being only about one-fifth greater. Nevertheless, as can be seen by comparing Curve 30, Fig. 2, obtained with nitrogen, and Curve 28, Fig. 2, obtained with steam, the steam acts specifically to maintain the catalytic activity. Subsequent analysis revealed that the catalyst charge had lost 64.5% of its total available oxygen in the nitrogen experiment whereas only 27.8% loss was incurred in the steam experiment. The inhibition of reduction by the excess steam is thus quite apparent.



Pig. 6.—Comparison of activities of MSA and CWS hopcalite in presence of steam in glass catalyst chambers. Curve 42—CWS hopcalite at 156°, 3:1 steam–gas mixture; Curve 44—MSA hopcalite at 175°, 3:1 steam–gas mixture.

Catalyst Poisons.—The absence of catalyst poisons in the converted water gas used in these tests was definitely proved by a series of tests with MSA hopcalite at the low temperature of 130° in which both purified and unpurified gases gave identical results. Purification was by means of hot reduced copper and chromic–sulfuric acid scrubbing. Comparison of the data for Tests 23 and 25, Fig. 5, obtained with unpurified gases and those shown in Test 26 with purified gases reveals no evidence of poisoning by the unpurified gases. The duplicability of results with different charges of the same catalyst is also illustrated by the results of these tests.

Activity of CWS Hopcalite in the Presence of Steam.—The effect of using the very active CWS catalyst in the presence of steam remained to be determined. A glass catalyst chamber was used. The conditions of the test were 156°, 3:1 steam–gas mixture, 1000-space velocity, composition of influent gas: 0.57% carbon monoxide, 0.6% oxygen, 74.1% hydrogen and 24.7% nitrogen. The data are plotted in Fig. 6, Curve 42. The efficiency remained over 96% during the entire test of seventy-seven hours.

A test with MSA hopcalite utilizing the same gas and other conditions as in the above experiment with CWS catalyst with the exception of a higher temperature of 175° is also plotted in Fig. 6, Curve 44. The efficiency after twenty-nine hours was 92%. The superiority of the CWS catalyst is here again quite evident.

Discussion

The Function of Steam.—Although previous investigators found that it was impossible to oxidize carbon monoxide in excess of 0.5% in the presence of hydrogen with moderate amounts of water vapor, it has here been demonstrated that in the presence of a large excess of steam it is possible to burn as high as 1.6%. With proper steam concentrations and temperature adjustment higher concentrations of 2–4% of carbon monoxide undoubtedly can also be handled. The functions of the steam are two-fold: (1) to dissipate rapidly the heat of reaction, thus preventing local overheating of the catalyst granules and (2) to specifically inhibit reduction of the catalyst and oxidation of hydrogen. The use of steam should permit the use of large catalyst beds and catalyst chambers built of poor heat-conducting materials.

The Decline in Activity.—The gradual decline in activity at the low temperature of 156° in the presence of three volumes of steam per volume of gas with 0.5–1.3% of carbon monoxide (Curves 28 and 17, Fig. 2) in converted water gas may have been due either (1) to the presence of catalyst poisons or (2) to a change in structure of the catalyst with decrease of active catalytic surface, most probably incurred through loss of oxygen.

The first of these possibilities is rendered improbable by the poisoning experiments cited above. The probable correctness of the second hypothesis is shown by the fact that, as can be seen in Table II, the activities decrease with increased loss of oxygen.

TABLE II

VARIATION OF ACTIVITY WITH OXYGEN LOST FROM CATALYST

Run number	32	28	17	30
% of total avail. oxygen lost	20.3	27.8	33.5	64.5
Efficiency of CO oxidation, %	98	89	86	57

It should be noted that no appreciable portion of the total carbon monoxide consumed in the 379-hour test run could have been furnished by the available oxygen in the catalyst. Calculation shows that the total available oxygen of the catalyst is equivalent to only 4% of the total carbon monoxide consumed.

In conclusion the author wishes to express his deep appreciation to Doctors E. C. White and P. H. Emmett for their kindly suggestions in the course of this work.

Summary

1. A study of the activity of a commercial hopcalite as a preferential carbon monoxide oxidation catalyst has shown that from 97 to 99% of the influent carbon monoxide may be oxidized catalytically by free oxygen in the temperature range of 160–195° from converted water gas of the composition: 1.3% carbon monoxide, 1.5% oxygen, 28.0% carbon dioxide, 49.0% hydrogen and 20.2% nitrogen, in the presence of three volumes of steam per volume of gas at 1000 dry gas space velocity.

2. A further study indicated that the catalyst always suffered a loss in available oxygen both through thermal dissociation and reduction by hydrogen and carbon monoxide. A decrease in the catalytic activity resulted from this loss of available oxygen.

3. The importance of rapid and efficient dissipation of the heat of reaction has been shown by tests with slightly moist gases in which very inefficient oxidations were obtained with hopcalite in poorly conducting glass catalyst containers while continued high efficiencies were obtained with a copper catalyst chamber.

4. The steam has the two-fold function of dissipator of reaction heat and inhibitor of reduction of the catalyst by hydrogen. The use of catalyst chambers constructed of good heat-conducting material would be of no added benefit in the presence of an excess of steam.

5. A comparison of the activities of commercial hopcalite and a laboratory scale preparation by the Chemical Warfare Service showed the former to be the less active.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 614]

FERRIC OXYBROMIDE HYDROSOLS

BY ARTHUR W. THOMAS AND EDNA R. HAMBURGER

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In a study of the behavior of ferric oxychloride hydrosols[1] previously reported[2] from this Laboratory, it was suggested that the nature of the anion was dominant in the behavior of hydrosols of this type. For example, while a ferric oxychloride hydrosol can be diluted with alcohol without precipitation of the dispersed phase, the addition of alcohol to a ferric oxysulfate hydrosol provokes instant precipitation. This is in accordance with the fact that chlorides in general are soluble in alcohol while sulfates are not. The above mentioned difference between ferric oxychloride and ferric oxysulfate hydrosols together with quantitatively measured behavior of ferric oxychloride sols on dialysis led to the contention that the stability of "ferric oxide" hydrosols resides in the solution forces of the ferric salts or of the basic ferric salts which are part of the colloidal aggregate.[2]

A chemical mechanism accounting for the precipitation of ferric oxychloride hydrosols by silicic acid–sodium silicate and arsenious sulfide–hydrogen sulfide hydrosols was also offered[3] showing that the chemical nature of all ions of a hydrosol must be reckoned with rather than merely considering the charge of the colloidal micelle. This idea is not new; Linder and Picton[4] in 1892 suggested that "the aggregates of ferric hydrate are held in solution almost entirely by their loose union with surrounding molecules of ferric chloride, themselves in a state of more perfect solution." In 1905 they concluded that the colloid was an hydroxychloride and not a hydrate associated with ferric chloride or free hydrochloric acid.

In this connection it is interesting to note that Freundlich and Wosnessensky[5] prepared a ferric oxide hydrosol by oxidizing a solution of iron carbonyl with hydrogen peroxide. Boiling the sol for a few minutes precipitated it; bubbling carbon dioxide through the coagulum repeptized it—this sol possesses the properties of a bicarbonate.

The present investigation was undertaken with the aim of extending

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[1] While sols of this type are generally described as hydrous ferric oxide peptized by certain cations, it is necessary in this paper as a result of certain differences in properties caused by the anion of the peptizing electrolyte, to include the name of the anion. The name hydrous ferric oxide sol may be applied accurately only in one case described in the literature, *i. e.*, the dispersion prepared and described by C. H. Sorum, THIS JOURNAL, 50, 1263 (1928).

[2] Thomas and Frieden, *ibid.*, 45, 2522 (1923).

[3] Thomas and Johnson, *ibid.*, 45, 2532 (1923).

[4] Linder and Picton, J. *Chem. Soc.*, *61*, 152, 165 (1892); 87, 1718 (1905).

[5] Freundlich and Wosnessensky, *Kolloid-Z.*, 33, 222 (1923).

the knowledge of the nature of "iron oxide" sols particularly from the angle of the "peptizing agent" which is responsible for and governs the stability and reaction of sols of the hydrous ferric oxide type. Ferric oxybromide sols were selected for this purpose.

Ferric oxybromide hydrosols have been known since **1859.** In that year Ordway[6] reported that "bromohydric acid takes up at least five equivalents of ferric oxyd" and Béchamp[7] that ferric bromide dissolves gelatinous ferric hydroxide as readily as ferric chloride. The work of these two investigators seems to constitute the only account of ferric oxybromide hydrosols in the literature.

Preparation

Since ferric bromide is not readily available, Béchamp's method could not be used. At first an attempt was made to prepare the sols by peptizing the freshly precipitated ferric oxide obtained from a Graham ferric oxychloride sol (by addition of ammonium hydroxide) with hydrobromic acid, reprecipitating with ammonium hydroxide and repeptizing with hydrobromic acid until chloride ion was absent. This method proved unsatisfactory due to the difficulty of removing all traces of chloride and the following procedure, the oxidation of ferrous bromide by hydrogen peroxide, was adopted. This is the same as Neidle's[8] method of preparing ferric oxychloride sols.

The details of the method are as follows: to each 100-g. portion of pulverized iron is added 500 cc. of 40% hydrobromic acid and one liter of distilled water. The mixture is heated gently and stirred constantly. As the rapid evolution of gas slows dawn somewhat the temperature may be raised. The reaction is assumed to be complete when the evolution of hydrogen ceases and oxidation to the ferric condition is just starting (as evidenced by traces of red, precipitated ferric oxide). The greenish-blue ferrous bromide solution is then filtered from the residual iron, carbon, etc., and oxidized by slowly adding hydrogen peroxide,[10] stirring constantly until ferrous ion test is negative. When approaching the end-point, the odor of free bromine is also observed. This free bromine is removed in the first twenty-four hours of dialysis.

Immediately after preparation, the sol is dialyzed against running water for twelve to twenty-four hours and then dialyzed against distilled water until the desired "purity" is obtained.

All sols dialyzing against distilled water, unless otherwise mentioned, were stirred by means of a current of compressed air washed with dilute sulfuric acid, dilute sodium hydroxide, passed through a column of glass beads and of absorbent cotton.

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[6] Ordway, *Am. J. Sci.*, [2] **26,** 197 (1859).

[7] Béchamp, *Ann. chim. phys.*, [3] **57,** 296 (1859).

[8] Neidle, THIS JOURNAL, 39, 2334 (1917).

[9] Pulverized iron (of 99.7 to 99.9% purity) kindly furnished by the Hawthorne Works of the Western Electric Company was used. According to analysis supplied by the donor, the following impurities were present: carbon, 0.022–0.058%; sulfur, 0.003–0.013%; silicon, 0.034–0.117%; manganese, 0.023–0 048%; phosphorus, 0.004–0.028%.

[10] The proprietary "Dioxygen" was used.

Tests with Laar's[11] reagent (sulfuric acid solution of diphenylamine) for the presence of bromate, peroxide, etc., gave negative results with sols prepared in this fashion.

Ferric oxychloride hydrosols were prepared in the same manner, using 100 g. of pulverized iron, 200 cc. of concd. C. P. hydrochloric acid and 1200 cc. of distilled water.

Analytical Procedure

The analytical results herein reported are expressed in terms of milli-equivalents per liter. In all cases analyses were made for total iron and total halide content.

Iron.—A portion of the sol evaporated to fuming with sulfuric acid to remove all bromine was then diluted, reduced in a Jones reductor in the customary manner and titrated with standardized potassium permanganate solution.

Halide.—To a portion of the sol 10 cc. of 16 M nitric acid, 10 cc. of 0.1 M silver nitrate and water were added to a volume of 125 cc. This mixture was heated overnight at about 60° in a dark place.[12] Check analyses made on potassium bromide solutions proved that no bromine was lost by this method.

Comparative Behavior of Ferric Oxybromide and **Ferric** Oxychloride Hydrosols.—A series of sols of varying Fe/halide ratios was prepared and the following properties measured: sodium sulfate liminal value, viscosity and electrical conductivity. While attention was concentrated upon the ferric oxybromide sols, a sufficient number of ferric oxychloride hydrosols were studied, however, to enable comparisons to be drawn between the two. All sols were "pressure" dialyzed in nitrocellulose bags against distilled water at room temperature until the desired ratio of iron to halide was obtained. They were then diluted to a concentration of about 400 milli-equivalents of iron per liter.

Since it was found that ferric oxybromide sols hydrolyze readily, they were used as soon as feasible after being prepared.

By liminal value is meant the average in millimoles of the amount of a salt which just fails to precipitate and the amount which just does precipitate the sol under given conditions. The technique adopted was as follows: into one series of test-tubes were pipetted 5-cc. portions of the sol, and in another series of tubes were placed 5-cc. volumes of salt solutions of varying concentration. The electrolyte solution was added to the sol by pouring slowly down the side of the tube and the contents were mixed by inverting twice. The tubes were then centrifuged for two minutes at 1300 revolutions per minute (radius, 28 cm.). The end-point was judged to be the tube in which the supernatant solution above the precipitate was clear and colorless, the supernatant solution of the tube just preceding being a pale yellow, and that of the tube following also being clear and colorless. The values in the tables are the averages of the readings of two series of measurements.

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[11] Laar, *Ber.*, 15, 2086 (1882).

[12] It is interesting to note that freshly prepared sols are thus decomposed much more readily than aged ones. The former are decomposed in the cold, whereas the latter require the elevated temperature for decomposition in the time mentioned.

Viscosity measurements were made at 25 ± 0.1° in an Ostwald viscometer. Readings are recorded as time of outflow, since the only significance which they have is a comparative one. The outflow time for water was 80.0 seconds.

The conductivity measurements were made at 25 ± 0.01° using a Freas cell with polished platinum electrodes, a circulary slide wire bridge and variable air condensers. The source of the alternating current was a Leeds and Northrup Vreeland oscillator. When not in use the cells were kept short-circuited as advised by Morgan and Lammert.[13] Parker and Parker's[M] revised value for the specific conductivity of 0.01 *N* potassium chloride was employed in determining the cell constant. Certain difficulties were encountered, rendering the experimental error about ±2.5%.

The results obtained for ferric oxybromide hydrosols are recorded in

TABLE I

FERRIC OXYBROMIDE HYDROSOLS. CHANGE IN PROPERTIES AS RATIO FE/BR INCREASES

Fe/liter, 415 milli-equiv. Maximum time elapsing between end of dialysis and final measurement, two weeks.

Sol[a]	Fe/Br, equiv.	Na_2SO_4, liminal value, millimoles	Viscosity, sec. outflow	Conductivity, mhos X 10^6
44	20.4	7.47	86.0	656
44A	22.2	7.15	87.2	*565*
44B	25.6	6.12	87.9	419
42A	25.7	5.96	89.4	...
44D	29.8	5.00	91.5	293
42	33.5	4.24	92.3	...
44C	38.5	3.65	..	166
43	41.8	3.62	93.9	...

[a] Sols 44, 44A, 44B, 44C and 44D were all made from the same mother sol by further dialysis. Sols 42 and 42A came from a different mother sol and Sol 43 from a third mother sol.

TABLE II

FERRIC OXYCHLORIDE HYDROSOLS. CHANGE IN PROPERTIES AS THE RATIO FE/CL INCREASES

Fe/liter, 415 milli-equiv. Maximum time elapsing between end of dialysis and final measurement. two weeks.

Sol[a]	Fe/Cl, equiv.	Na_2SO_4, liminal value, millimoles	Viscosity, sec. outflow	Conductivity, mhos X 10^6
11	20.0	5.05	90.4	279
11F	23.1	3.94	92.3	218
11A	24.0	3.94	92.5	195
10	25.7	3.49	91.6	...
11E	30.3	2.67	92.0	153

[a] Sols 11, 11A, 11E and 11F were all prepared from the same stock sol, and Sol 10 from a second stock sol.

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[13] Morgan and Lammert, THIS JOURNAL,, **45**, 1672 (1923); **46**, 1117 (1924).

[14] Parker and Parker, *ibid.*, 46, 312 (1924).

Table I and plotted in Fig. 1. Similar results for ferric oxychloride hydrosols are given in Table II and in Fig. 1.

The measurements charted in Fig. 1 were not carried beyond the ratio Fe/Cl = 30 due to irregularities caused by incipience of precipitation in the ferric oxychloride sols. Incipience of precipitation is not observed in ferric oxybromide hydrosols until the Fe/Br ratio is much greater.

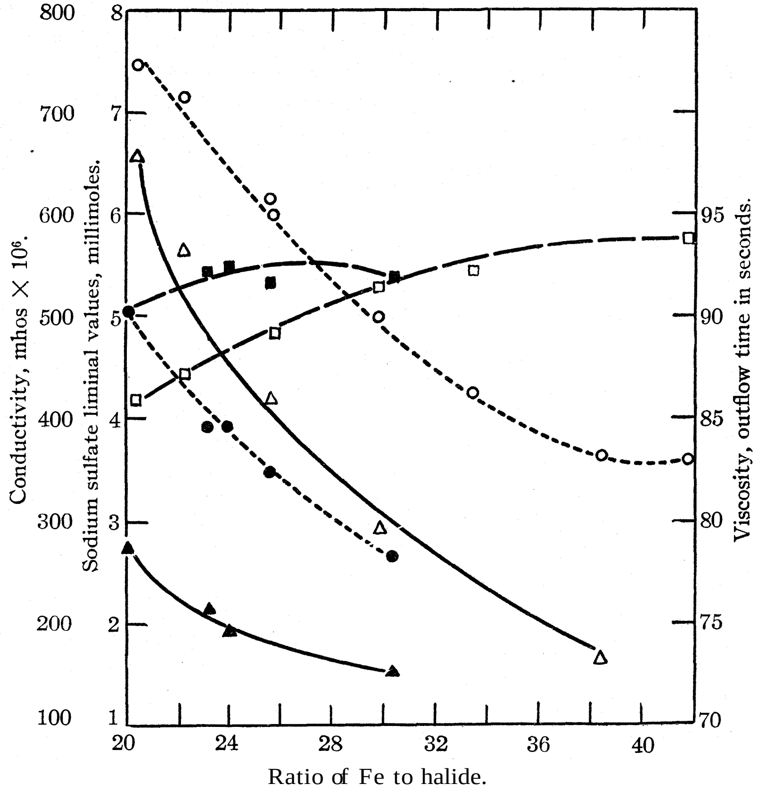

Fig. 1.—Variation of certain properties with variation of Fe : halide ratio. ●, **Liminal** values, ferric oxychloride sols; O, liminal values, ferric oxybromide sols; ■, viscosities, ferric oxychloride sols; O, viscosities, ferric oxybromide sols; ▲, conductivities, ferric oxychloride sols; A, conductivities, ferric oxybromide sols.

It is seen that as the Fe/halide ratio increases, the conductivity and sodium sulfate liminal value decrease, while the viscosity increases in each case. In every case, however, at a given Fe/halide ratio the conductivity of a ferric oxychloride hydrosol is less than that of a ferric oxybromide sol, and the dispersed phase of a "chloride" sol is more easily salted out by sodium sulfate than the dispersed phase of a "bromide" sol.

Pairs of ferric oxybromide and oxychloride hydrosols were dialyzed simultaneously as nearly as possible to the same Fe/halide ratio and the concentrations then adjusted so that they were identical in each pair. Liminal values were then determined for sodium chloride, sodium bromide and sodium hydroxide, using the technique previously described. In order to obtain a sharply defined precipitate it was necessary to centrifuge the coagula caused by sodium chloride and sodium bromide for three minutes. For purposes of comparison, the liminal values for sodium sulfate are repeated from the previous tables. The results obtained are reported in Tables IIIA and IIIB.

TABLE III

LIMINAL VALUES FOR ELECTROLYTES ON FERRIC OXYCHLORIDE AND FERRIC OXYBROMIDE HYDROSOLS OF CORRESPONDING FE/HALIDE RATIO

A. SOLS PREPARED BY ROOM TEMPERATURE DIALYSIS

Sol	Fe/halide equiv.	Millimoles/liter NaCl	NaBr	Na_2SO_4	NaOH	$K_4Fe(CN)_6$
Cl-10	25.7	162	395	3.49	6.76	..
Br-42A	25.5	320	644	5.96	11.7	..

Fe/liter = 415 milli-equiv.

B. SOLS PREPARED BY HOT DIALYSIS

Sol	Fe/halide equiv.	Millimoles/liter NaCl	NaBr	Na_2SO_4	NaOH	$K_4Fe(CN)$
Cl-4P2	23.7	202	324	4.45	...	3.13
Br-37	24.4	381	787	6.37	...	3.25

Fe/liter = 440 milli-equiv.

The data in Table III show in general that ferric oxybromide sols are less easily salted out than corresponding[15] ferric oxychloride sols.

Aging Experiment.—Ferric oxybromide hydrosols when freshly prepared are clear brownish-red when viewed by either reflected or transmitted light. It was noticed that after such sols stand at room temperature for about six months they assume a turbid appearance to reflected light while still clear brownish-red to transmitted light. From past experience with ferric oxychloride sols in this Laboratory, it is known that the latter undergo such a change only after several years' standing.

Repeatedly in the preparation of these sols it has been noticed that ferric oxychloride hydrosols require at least twice the time to reach a given Fe/halide ratio by dialysis that ferric oxybromide sols do, thus indicating a greater rate of hydrolysis of the latter. Evidence for greater degree of hydrolysis is suggested by the fact that while ferric oxychloride sols of the concentration and Fe/Cl ratio studied here show a P_H value of 4.9,[2] the P_H value of similar freshly prepared ferric oxybromide hydrosols is indicated to be about 3, by means of the quinhydrone electrode, taking initial potentials.

[15] The word *corresponding* is used *here* and subsequently to mean hydrosols of the same total iron content and like ratio of total iron to total halide.

Several hydrosols were submitted to accelerated aging by enclosing in securely stoppered pyrex glass containers which were placed in an oven at 90 ± 2°. The results for two hydrosols are recorded in Tables IV and V and in Fig. 2.

The increase in conductivity and the decrease in viscosity upon heating indicate that the micelles undergo hydrolysis and dehydration. Comparing the curves for the two sols, it is seen that ferric oxybromide hydrosol micelles hydrolyze much more rapidly than ferric oxychloride micelles.

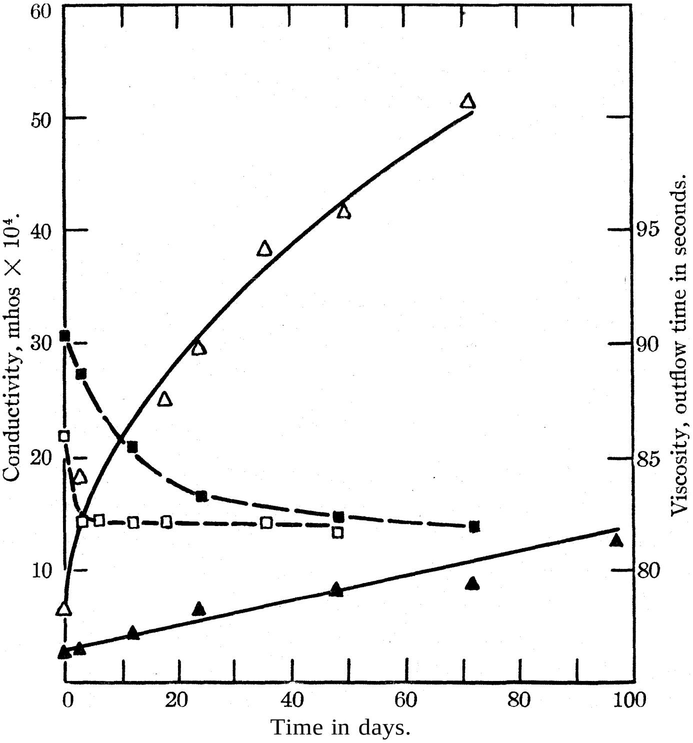

Fig. 2.—Change in certain properties as *a* function of time at 90°.
■, Viscosity, ferric oxychloride sol; □, viscosity, ferric oxybromide sol; ▲, conductivity, ferric oxychloride sol; A, conductivity, ferric oxybromide sol.

It will be recalled that the data in Tables I and II indicate that ferric oxybromide sols are hydrolyzed to a greater extent than corresponding ferric oxychloride sols.

Since the viscosity of a given ferric oxyhalide sol varies with degree of hydrolysis, it is evident that the ratio of iron to halide is insufficient for exact definition of a hydrosol of this type.

Greater hydrolysis of the dispersed phage results in micelles richer in

TABLE IV

AGING OF FERRIC OXYBROMIDE HYDROSOL NO. 44[a]

Heated, hours	Appearance[c]	Visc., sec. outflow	Cond., mhos × 10^5
0	A	86.0	66
3	B	82.1	183
12	B	82.1	
18	D	82.1	250
24	E	81.7	295
36	F	82.1	383
48	G		419
72	G		514
90	H		. .

[a] The concentration was 416 milliequivalents of Fe per liter; ratio Fe/Br = 20.4.

TABLE V

AGING OF FERRIC OXYCHLORIDE HYDROSOL NO. 11[b]

Heated, hours	Appearance[c]	Visc., sec. outflow	Cond. mhos × 10^5
0	A	90.4	28
3	B	87.6	29
12	B	85.0	45
24	B	83.3	63
48	C	52.4	83
72	F	. .	89
97	G	. .	125
120	G	. .	131
1 month	H	. .	

[b] Same concentration as Sol 44; ratio Fe/Cl = 20.0.

[c] The key letters under "appearance" have the following significance: A, characteristic color; B, redness of characteristic color intensified; C, B plus slight yellow precipitate; D, brownish turbidity to reflected light just starting; E, chocolate brown to reflected light, clear red brown to transmitted light; F, chocolate or orange brown somewhat turbid to transmitted light, yellow sediment; G, orange, absolutely opaque, usually a layer of clear red sol above and a layer of yellow sediment; H, complete precipitation, orange, finely divided solid covered with clear supernatant liquor which gives a positive test for halide ion.

ferric oxide and poorer in halide, and consequently less stable, yet more sodium sulfate is required for the salting out of ferric oxybromide sols than for corresponding ferric oxychloride sols despite the greater hydrolysis of the former, thus showing the significance of the anion or anionogen upon the properties of sols of the ferric oxide type.

Summary

1. As the ratio of iron to halide in ferric oxybromide and ferric oxychloride hydrosols diminishes, the viscosity increases while the liminal value and electrical conductivity decrease.
2. Ferric oxybromide sols have higher electrical conductivities than corresponding ferric oxychloride sols.
3. The micelles of ferric oxybromide sols appear to hydrolyze more readily and to a greater extent than those of corresponding ferric oxychloride sols.
4. The dispersed phase of ferric oxychloride sols is more easily salted out than that of the corresponding ferric oxybromide sols.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY MEDICAL COLLEGE, NEW YORK CITY]

A NOTE ON THE DETECTION AND ESTIMATION OF COBALT IN PRESENCE OF NICKEL

BY ABRAHAM LIEBERSON

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The methods to be described provide for the colorimetric detection of cobalt in the presence of 300 to 400 times its weight of nickel, and for the rapid and accurate colorimetric determination of 0.5 mg. (or 0.25 mg.) of cobalt in the presence of as much as 10 times its weight of nickel. Since nickel and cobalt are readily separated from other metallic ions, the method should prove useful, although, as will be detailed later, certain other cations give a reaction similar to that of cobalt.

The colorimetric reaction employed is the reduction by cobalt of arsenophosphotungstic acid in presence of cyanide whereby intensely blue tungstous acid is formed and the cobalt is oxidized to cobalticyanide. Under identical conditions nickel fails to reduce the complex tungstic acid reagent.

Solutions Required

1. Reagent.—The arsenophosphotungstic acid[1] is prepared by placing 100 g. of pure sodium tungstate in a liter pyrex flask and dissolving in about 600 cc. of water; **50** g. of pure arsenic acid (As_2O_5) is now added, followed by **25** cc. of 85% phosphoric acid and **20** cc. of concentrated hydrochloric acid, as condensing agent. The mixture is boiled for twenty minutes, cooled and diluted to one liter. The reagent appears to keep indefinitely.

2. Sodium Cyanide.—A 5% solution of sodium cyanide, to which 2 cc. of concentrated ammonia have been added per liter. This solution should be prepared fresh about every two months.

3. The standard cobalt solution, containing **0.5** mg. of cobalt in 10 cc. of solution, is prepared by dissolving in a liter of distilled water **1.25** g. of pure $CoCl_2 \cdot H_2O$, or **2.02** g. of $CoCl_2 \cdot 6H_2O$ or **2.47** g. of $Co(NO_3)_2 \cdot 6H_2O$. To obtain the standard, the solutions are diluted **1:10** before using.

For the qualitative detection of cobalt the following procedure is best. To 5 cc. of unknown solution in a test-tube add **2** cc. of the arsenophosphotungstic acid reagent, followed by 2 cc. of the 5% sodium cyanide; **0.01** mg. of cobalt gives immediately a recognizable blue color. Nickel, unless present in such concentration as to obscure a faint blue color by its dark green shade, does not interfere with this color test. Thus **0.01** mg. of cobalt can be detected in the presence of **2** or **3** mg. of nickel. Stannous tin, manganese, ferrous iron, mercurous mercury, copper and sulfide are interfering ions and must not be present. The fact that nickel does not react with the reagent permits the testing of nickel salts by this method for the presence of cobalt and iron as impurities. This qualitative test is made as follows. Add to **5** cc. of approximately 1% nickel salt, **3** cc. of reagent and enough 5% sodium cyanide just to redissolve the nickel cyanide that is first formed on the addition of the cyanide. An immediate blue or greenish-blue solution is formed if iron or cobalt is present.

The method for the estimation of cobalt in the presence of nickel is as follows.

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[1] S. R. Benedict, *J. Biol. Chem.* **51, 187 (1922).**

To 10 cc. of approximately neutral cobalt solution containing about 0.5 mg. of cobalt, and also to 10 cc. of standard cobalt solution containing exactly 0.5 mg. of cobalt,[2] add 3 cc. of arsenophosphotungstic acid reagent. Invert once. Add 4 cc. of the cyanide solution from a buret. Invert both tubes once simultaneously. Compare the standard and unknown blue solutions in a colorimeter. For best results the colorimetric reading should be made from two to ten minutes after inversion of the tubes. The ratio of the reading of the standard to the reading of the unknown, multiplied by 0.5 gives the mg. of cobalt in 10 cc. of unknown solution. The colors obtained match exactly. No turbidity develops even after twenty-four hours of standing. Nickel does not interfere with this test except that if the 10 cc. of solution contains more than 5 mg. of nickel, nickel cyanide tends to be precipitated when the cyanide is added. If more cyanide is used (*i. e.*, 6–8 cc.), more nickel can be kept in solution, but the tendency to turbidity is increased. In the presence of up to 5 mg. of nickel, the readings are accurate to within about 1% (0.005 mg. of cobalt). The ions mentioned above which interfere with the qualitative reaction must be absent. There is another group of metallic ions which, although not giving the test directly, may interfere if present in appreciable amounts (*i.e.*, more than 4 or 5 times the concentration of cobalt) by yielding a turbid solution. This group includes NH_4, Mg, Ca, Sr, Ba, Sn, Sb, As, Cd, Bi, Pb, Ag. Finally, it should be noted that colored solutions of manganese and chromium obviously interfere with the proper color readings between standard and unknown.

The essential accuracy of this method was demonstrated by the determination of the cobalt present in pure cobalt solutions and in potassium cobaltinitrite precipitates (after converting the cobaltinitrite to a cobaltous salt by heating with *N* hydrochloric acid. The results obtained in a long series of determinations in the latter case showed a maximum deviation from the theoretical of 1.5%, with an average deviation of about 0.5%.

In conclusion the writer wishes to express his indebtedness to Professor S. R. Benedict, whose help has been essential to the completion of this work.

BROOKLYN, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

SOME NEW EXPERIMENTS ON THE CHEMICAL EFFECTS OF X-RAYS AND THE ENERGY RELATIONS INVOLVED

BY GEORGE L. CLARK AND LUCY W. PICKETT

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Although the photochemical action of x-radiation is of interest because of its possible significance in interpreting the physiological effects, very few studies in this field have been made until recently. Within the last two years, however, the oxidation of ferrous to ferric sulfate has been studied by Fricke and Morse,' oxyhemoglobin to niethemoglobin by Fricke and Petersen,[2] the inversion of sugar by Reinhardt and Tucker,[3] and the

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[2] If less than 0.5 mg. of cobalt is available, the volume of solution and of reagents used can be reduced correspondingly.

[1] Fricke and Morse, ***Am.* J.** *Roentgenology & Radium Therapy, 18,* 426–430 *(1927).*

[2] Fricke and Petersen, *ibid.*, **17,** *611420 (1927).*

[3] Reinhardt and Tucker, *Radiology,* 12, *161–153 (1928).*

decomposition of iodoform,[4] hydrogen peroxide and potassium persulfate[5] by Glocker. These researches have established the facts that the photochemical action is very small and is independent of the wave length of the radiation within limits of about 0.2 to 0.8 Å. Studies of the coagulatory action of x-rays on colloids have been carried on recently by Fairbrother and co-workers.[6]

TABLE I

RESULTS OF EXPERIMENTS ON CHEMICAL EFFECTS OF X-RADIATION OF EFFECTIVE WAVE LENGTH 0.24 Å.

Initial substance	Change	Remarks
Anthracene	No change in 200 hours	
Dianthracene	No change in 200 hours	
Maleic acid	No change in 200 hours	
Fumaric acid	No change in 200 hours	
Iodine and benzene	Absorption of iodine 6.5%	
Ferrous sulfate	40% oxidation to ferric	Agreement with Fricke's result
Ferric sulfate	No change	Kailan reported slight reduction by radium rays
Potassium iodide	Iodine freed	Quantitative results below
Potassium nitrate	O_2 and KNO_2	
Potassium iodate	I_2 and KI	Reported by Chamberlain
Potassium permanganate	MnO_2	Reduction to Mn^{++} noted by Chamberlain
Methylene blue in acetone	No change	
Sucrose	Slight inversion	Effects of presence of colloidal lead and lead nitrate, and of simultaneous irradiation with ultraviolet and x-rays presented below
Dyes	No change	
Triphenylmethane		
Diphenylmethane		
Azoindigo		
Condensation		
Benzaldehyde + benzaldehyde		5% in 5 hours of raying
Benzaldehyde + acetophenone		35%
4-Hydroxy-benzaldehyde + acetophenone		75%
4-Hydroxy-benzaldehyde + benzaldehyde		19%
Acetone + acetaldehyde		Very small
Piperonal + acetophenone		14%
Colloid coagulation		
Pb	Stabilized	
Albumin	Coagulated	
Clay	Coagulated	Pure kaolin unaffected

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[4] Baumeister and Glocker, Z. *physik. Chem.*, **97**, 368 (1921).

[5] Glocker and Risse, *Z. Physik*, **48**, 845–851 (1928).

[6] Crowther and Fairbrother, *Phil. Mag.*, [7] **4**, 325–335 (1927); Fairbrother, *Brit J. Radiology*, [N.S.] *1*, 121–125 (1928); *Phil. Mag.*, [7] *6*, 385401 (1928).

The present researches were undertaken in order to determine what types of reactions are sensitive to radiation and, secondly, to study the energy relations involved. In order to satisfy the first point, a number of reactions were investigated. The procedure followed in general was to expose the specimen in a thin-walled pyrex bulb to polychromatic radiation from a tungsten target of effective wave length 0.24 Å. at a distance of eight inches from the focal spot. In each case a control of a similar bulb treated in the same manner but protected from radiation by a lead shield was used. The qualitative results obtained are shown in Table I.

Details of Experiments on Chemical Changes by X-Rays

Ferrous Sulfate ⟶ Ferric Sulfate.—A 10-cc. solution of ferrous ammonium sulfate in 0.04 N H_2SO_4 was exposed to x-rays from a molybdenum tube for twenty hours and then titrated with 0.01010 $KMnO_4$: exposed, 8.18 cc. required; blank, 5.85 cc. required. Experiments in which sealed bulbs of ferric sulfate were given exposures of several months gave negative results.

Anthracene ⟶ Dianthracene.—A saturated solution of anthracene in phenetole was exposed to radiation for forty-six hours with no effect.

A saturated solution of anthracene in xylene was exposed for several hours to ultraviolet light from a mercury arc in quartz and a considerable precipitate of dianthracene was formed. A portion of the original solution of anthracene sealed in a bulb, and a second bulb containing a suspension of the dianthracene formed in xylene, were exposed to over 150 hours of raying and no apparent change in either took place.

Iodine and Benzene.—A solution of iodine in benzene sealed in a bulb was exposed to x-rays. One-cc. samples of this and of a similar sample unexposed were titrated with sodium thiosulfate. Results—cc of 0.10 N $Na_2S_2O_3$ used: unexposed, 35.70, 35.70; exposed, 32.37, 32.27.

Acetone, Iodine and Water.—Apparently unaffected by x-rays. The high temperature coefficient makes this reaction impracticable for study.

Inversion of Sugar in the Presence of Lead Nitrate.—The presence of lead nitrate apparently aids the inversion of sugar under the action of x-rays but the effect is probably secondary due to a change in P_H. Results obtained after twenty-three hours of exposure to radiation from a tungsten target tube at 75,000 volts and 4 to 5 milliamperes lasting over an interval of one week were as follows.

Solution	Saccharimeter reading at 20°	P_H
Sugar solution unexposed	38.8	5.8
Sugar solution exposed to x-rays	38.4	5.8
100 cc. of sugar solution +1 cc. of 10% $Pb(NO_3)_2$	38.2	5.8
100 cc. of sugar soln. +1 cc. of 10% $Pb(NO_3)_2$ exposed to x-rays	36.4	$4.4 < P_H < 5.2$

Condensations of Aldehydes and Ketones

Reactions in the field of organic chemistry offer many opportunities for the study of the effects of x-radiation with the possibility that much larger changes may be observed than in the examples of inorganic compounds thus far considered. As one promising type was chosen the condensation reaction of aldehydes and ketones, particularly on account of the known photochemical reactions of formaldehydes to form sugars. Claisen and Claparède[7] prepared phenylstyryl ketone by mixing benzaldehyde and acetophenone in equal proportions, saturating with hydrogen chloride gas and allowing to stand in the cold for twelve hours. The hydrogen chloride was then removed from the product by heating the mixture on the water-bath for several hours. The ketone so produced was crystallized from petroleum ether with a yield of **32%.** While this reaction has the disadvantage that it will proceed without radiation, it was thought that there might be a distinct catalytic effect in irradiation. Accordingly two samples of each of the several mixtures were placed in exactly the same place, at 50°, one being entirely protected by lead as a control and the other exposed to x-rays from a tungsten target tube with an effective wave length of 0.24 Å. for a period of five hours.

RESULTS OF SERIES OF EXPERIMENTS

No.	Aldehyde	G.		G.	HCl	Product			
						Exposed to x-rays		Control	
						G.	%	G.	%
1[a]	Benz-	15	Acetophenone	15	2 g.	10.5	35	7.0	23
2	4-OH-Benz-	1	Acetophenone	1	5 drops	1.5	75	1.2	60
3	4-OH-Benz-	1	Benzaldehyde	1	5 drops	0.38	19	0.27	13.5
4[b]	Benz-	30	......	..	1 cc. (concd.)	1.5	5	1.4	4.7
5"	Piperonal	5	Acetophenone	Excess	10 drops	1.4	14	0.6	6
6	Acetal-	..	Acetone.—Two samples were treated in similar manner but only a small amount of dark red oil was formed, probably due to the formation of para-acetaldehyde.						
7	Salicyl-	..	Acetophenone.—The product formed only with exposure to x-rays is a dark red oil, and not chalcone, which the usual condensation gives. The oil could not be crystallized from alcoholic solution.						

[a] Benzaldehyde + acetophenone ⟶ phenyl styryl ketone ($C_6H_5CH{=}CHCOC_6H_5$).

[b] Melting point of product 125°, probably stilbene, $C_6H_5CH{=}CHC_6H_5$.

[c] Melting point of product (both) 119–120°, colorless needles.

Summarizing the results of these reactions, it may be concluded that the condensation of aldehydes with ketones is markedly catalyzed by x-radiation, while the condensation of aldehyde with aldehyde is affected not at all or to only a small extent by the rays.

It is evident from many of these results that sensitivity to ultraviolet light is no criterion for prophesying a sensitivity to radiation in the region of 0.2–0.3 Å. The second conclusion to be noted is that the reactions most affected are those which involve oxidation in aqueous solution.

The above results shed no light on the question of the physiological action of x-rays. No chemical action yet studied, with the exception of the reduction of the silver bromide on a photographic plate, the oxidation of ferrous sulfate and possibly of the new aldehyde and ketone conden-

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[7] Claisen and Claparède, *Ber.*, 14, 2463 (1881).

sation reactions presented in this paper, is of the same order of magnitude as that change which occurs in body tissue. It is possible that some chemical reaction sensitive to radiation, whose counterpart has not yet been discovered, may underlie physiological action, or that the latter depends on such an effect as the coagulation of a colloid. Several examples of the latter were investigated such as the coagulation of egg albumin and of colloidal clays, which give changes of larger magnitude than those observed in the case of chemical reactions. Further studies were discontinued inasmuch as several recent papers by Fairbrother have appeared on the subject.

A Test of the Theory of Hydrogen Peroxide Formation in the Photochemical Oxidation of Potassium Iodide and the Reduction of Potassium Nitrate

Inasmuch as experiments by Glocker have shown that x-radiation influences the decomposition and also the formation of hydrogen peroxide, it seemed possible that the oxidations noted in aqueous solution were merely secondary reactions following the production and subsequent decomposition of hydrogen peroxide from water and oxygen, The following set of experiments was designed to test this hypothesis.

1. Two thin-walled pyrex tubes were filled with a 2% potassium iodide or 0.1 *M* potassium nitrate solution. Through the following devices one was kept saturated with oxygen while the other was freed of the gas, and both were exposed to the same dose of radiation.

(a) One was boiled to expel oxygen, cooled in a nitrogen atmosphere and sealed. The other was provided with an outlet into an absorption bulb of potassium iodide not exposed to the radiation, and a slow stream of oxygen or air bubbled through during the exposure.

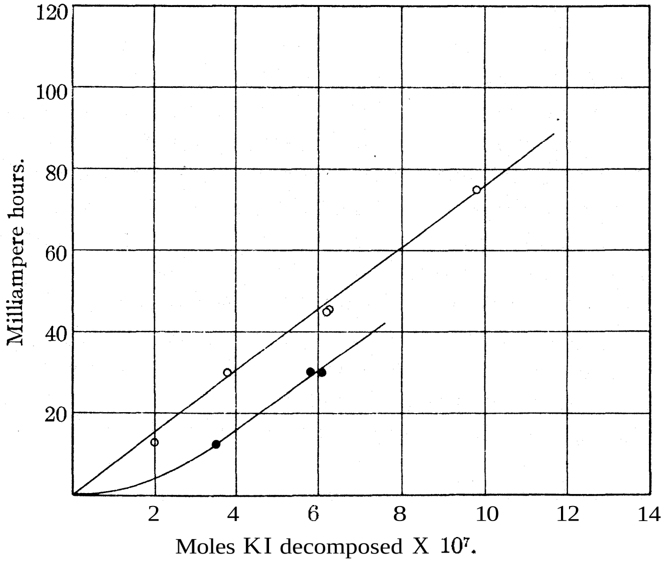
(b) One was heated at 100° to expel oxygen and sealed at that temperature; the other was saturated with oxygen at 0° and sealed.

The experimental data, which are illustrated by the accompanying graph, Pig. 1, revealed the following facts. (1) The decomposition of potassium iodide in the absence of oxygen is a straight line function of the dosage of radiation. (2) The decomposition of potassium iodide in the *presence* of an excess of oxygen takes place to a larger extent, and is not in direct proportion to the amount of radiation. (3) The decomposition of potassium nitrate is a straight line function of the dosage of radiation, and is independent of the presence of oxygen. (4) The ratio of molecules of potassium nitrate to molecules of potassium iodide decomposed by the same amount of radiation is 2.90.

The following conclusion might, therefore, be drawn from the data: the decomposition of potassium iodide in the first case (absence of oxygen) is independent of any hydrogen peroxide mechanism which requires the presence of oxygen. Even if the objection should be raised that a very slight amount of oxygen might have been retained by the water under experimental conditions, the direct proportionality between dosage of radiation and amount of change would indicate that the concentrations of the initial reactants do not change appreciably, a condition which is true for the water and potassium iodide but not for the oxygen. The reaction occurring would seem to be

$$KI + H_2O = KOH + I + {}^1/_2H_2$$

Though this reaction would involve a large increase in free energy, the amount of energy absorbed in the radiation is much greater. The production of hydrogen from water under the radiation by x-rays has been noted by Fricke.



○, In absence of oxygen; ●, in presence of oxygen.

Fig. 1.

In the presence of excess oxygen, however, there is a possibility of the formation and subsequent decomposition of hydrogen peroxide suggested by Glocker, and consequent freeing of iodine. This effect might either supplant or merely add to the reaction discussed above; in either case more iodine would be freed, and the relation between dosage and chemical change might not be linear. This conclusion is consistent with the experimental data.

The same reasoning shows that the decomposition of potassium nitrate is independent in any case of the hydrogen peroxide formation. The reaction occurring is $KNO_3 = KNO_2 + {}^1/_2O_2$. This is consistent with the tact that hydrogen peroxide does not affect a solution of potassium nitrate but oxidizes a solution of potassium iodide.

Thus it is concluded that the mechanism of the formation and subsequent decomposition of hydrogen peroxide is not essential for oxidation in aqueous solutions. In certain special cases, however, it may play a contributory part in the total effect.

In connection with the above results, tests were made for the presence of ozone and hydrogen peroxide. A stream of oxygen saturated with water vapor was allowed to flow past a thin glass window which was exposed to radiation. The gas was then passed into an absorption tube containing potassium iodide solution. No trace of free iodine was found after an exposure of fifteen hours, during which time 12 liters of oxygen passed the window, thus indicating that the formation of ozone, unless immediately decomposed, occurred to a negligible extent.

In order to test for hydrogen peroxide, a tube of distilled water was exposed to radiation for nine hours and opened into a solution of potassium iodide. No free iodine was detected. Glocker reports the detection of a small amount of hydrogen peroxide under similar circumstances. Inasmuch as radiation has been conclusively shown to cause the decomposition of hydrogen peroxide, it is probable that a small amount may have formed and decomposed before detection.

Experiments with Simultaneous Irradiation by Ultraviolet Light and X-Rays

Some recent evidence has been obtained in this Laboratory that the physiological effects of x-rays, for example, on fungi are accentuated by previous or simultaneous ultraviolet irradiation; in other words, the effects of the two kinds of rays are not additive. It was then thought advisable to test this observation with inorganic substances.

Two similar quartz weighing bottles containing 12 cc., each filled with 0.01 M potassium iodate are arranged so that the light from a mercury arc lamp is evenly distributed between them. One is in the path of x-rays, from which the other is shielded by a lead screen. The temperature coefficient of the reaction is low, but the temperatures are maintained as nearly equal as possible by cooling with a stream of water or of air from two equal openings in the same nozzle. Inasmuch as there is no procedure suitable for directly determining such small amounts of iodine and potassium iodide in the presence of potassium iodate, the following method was adopted: 10 cc. of the reaction mixture was shaken in a separatory funnel with chloroform. The chloroform layer was drawn off and the residue weakly acidified with 0.4 cc, of N sulfuric acid. Under these conditions the potassium iodide and potassium iodate react to give iodine, which is extracted with chloroform. The extracts are titrated with 0.001

N sodium thiosulfate. In a run of three and one-half hours at 70 k. v. and 5 m. a., the following results were obtained

		U. v.	U. v. + x-rays	x-rays
Cc. of 0.001 *N* thiosulfate used	I	0.20 cc.	0.13 cc.	....
	KI	0.10 cc.	0.20 cc.	....
	Total	0.30 cc.	0.33 cc.	0.03 cc.

In two other experiments, where the difference was measured qualitatively by the depth of color in the chloroform layer, the potassium iodide was found to be appreciably greater in the tube subjected to x-rays, while the iodine formed in the two cases seemed to be about the same with a little more perhaps in the ultraviolet alone. Apparently the effects of ultraviolet light and x-rays in this case are, within experimental error, additive. The mechanism of this complicated decomposition as shown by the distribution between iodine and potassium iodide is evidently affected. The additive effect has been further verified more directly in the photolysis of potassium nitrate.

Energy Relations in the Photolysis of Potassium Nitrate by X-Rays

A study has been made of the energy relationships involved in the photolysis of potassium nitrate by x-rays. This reaction has been the subject of much study in connection with the photochemical action of ultraviolet light. The unfiltered radiation from a tungsten target Coolidge tube, operating at 105 k. v. as measured by a sphere gap and 3 m. a., was used in this work. The effective wave length, measured by the Duane method, which involves the determination of the thickness of aluminum which has the same absorbing power as 1 mm. of copper, was found to be 0.236 . The intensity and dosage in "*r*" units[9] of the radiation were measured by a small air wall ionization chamber constructed of Acheson graphite which analyzed as containing 0.2% impurity, and an electrode of aluminum which contained 0.3% iron. The walls of the chamber were 1 mm. thick and the volume 0.999 cc. The saturation current was measured by a Lindemann electrometer calibrated with a standard cell. The solutions used were of 0.01 M potassium nitrate contained in pyrex glass bulbs which were blown with thin-walled flat sides. Intensity measurements were made of the incident radiation and of the radiation which had passed through the solution. From measurements of the total area exposed the total amount of energy absorbed could be computed. The solutions

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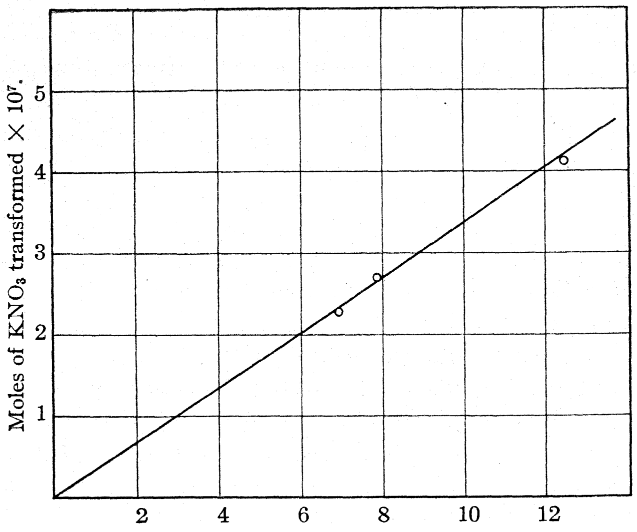
[8] Clark, "Applied X-Rays," McGraw-Hill Book Co., New York, 1927, p. 25.

[9] The international "*r*" unit adopted by the International Congress of Radiology at Stockholm in 1928 is the quantity of x-radiation which, when the secondary electrons are fully utilized and the wall effect of the chamber is avoided, produces in 1 cc. of atmospheric air at 0° and 76 cm. of mercury pressure, such a degree of conductivity that one electrostatic unit of charge is measured at saturation current.

were analyzed for nitrite by the Warburg method as modified by Villars,[10] using weight burets and 0.001 N thiosulfate.



Total energy absorbed in *r* units ÷ 36,000.
Fig. 2.

The results of three entirely independent experiments illustrated in Fig. 2 are as follows:

Expt.	Exposed area, cm.^{2}	Thickness of layer, cm.	Weight of 0.001 *N* thio, g.	Incident energy per cm.^{2} per sec., *r*	Energy absorbed per cm.^{2} per sec., *r*
1	15.48	1.62	0.4117	2.56	0.80
2	15.90	1.04	.2702	2.32	.490
3	12.91	1.12	.2291	2.40	.535

Total energy absorbed (10 hrs.)	Molecules reacting per *r* unit	Molecules per ion pair (*M/N*)	Energy cal./mole
445,680 *r*	5.58×10^{11}	0.2–0.3	1.31×10^7
280,476 *r*	5.83×10^{11}	0.2–0.3	1.25×10^7
248,400 *r*	5.58×10^{11}	0.2–0.3	1.31×10^7

Fairbrother makes the assumption that a given amount of radiation will produce approximately the same number of ion pairs in a dilute aqueous solution as are produced in the same weight of air, inasmuch as the atomic numbers of air and water are not very different. To allow for relative densities of air and dilute solution, a factor of about 1000 is involved. If this assumption is adopted, the number of molecules of potassium nitrate which react for each ion pair may be calculated

[10] Villars, THIS JOURNAL, **49**, 326–337 (1927).

$\frac{\text{total energy}}{\text{charge on electron}}$ = no. ion pairs per cc. in air $= \frac{10^{10}}{4.774} = 2.1 \times 10^9$ ion pairs per cc. in air, or approximately 2×10^{12} ion pairs per cc. in the solution;

$\frac{\text{no. molecules reacting}}{\text{no. ion pairs}}$ = molecules per ion pair

Using the data given above, the values for the latter are between 0.2 and 0.3 for this endothermic decomposition of potassium nitrate. The number of molecules per ion pair may be calculated independently from the energy in calories per mole and the work required to form one ion pair (35 volts): $(1.313 \times 10^7$ cal./mole $KNO_3)/(23{,}000 \times 35$ cal./mole ion pairs), or approximately 0.1 molecule of potassium nitrate per ion pair. This is in satisfactory agreement with the value calculated above, considering experimental difficulty, and with the order of magnitude to be expected thermodynamically.

In order to express results in terms of absolute energy, the absorption coefficients and the fraction of the absorbed energy which is converted into the kinetic energy of electrons and thence into the work of formation of ions must be known. The absorption coefficient, 0.228, as calculated from the above data agrees very closely with the value for absorption of the same wave length in water interpolated from a series of values given by Glocker.[5] The fraction of the total absorbed energy converted into work of formation of ions is the ratio of the values of the absorption coefficients for the energy given to recoil and photoelectrons to that of the total absorption coefficient. Using values recorded by Glocker, this fraction for the effective wave length used is 0.263.

The absorbed energy as measured in *r* units may be converted into ergs by the use of the formula proposed by Rump[11] and Kulenkampff's[12] experimental value of 35 volts as the work required to form one ion pair in air

$$\frac{E}{i} = \frac{\epsilon}{0.36}\left(\frac{\rho}{\tau + \sigma_v}\right)$$

where $E/i = 1944$ ergs/r unit, ρ = density, $\epsilon = 35$ volts and $\tau + \sigma_v$ = absorption coefficient attributed to recoil and photoelectrons.

Thus the total energy absorbed in Expt. 1 is $445{,}680 \times 1944$ ergs, the fraction 0.263 of which is transformed into work of ionization. At the same time 4.117×10^{-7} moles of potassium nitrate are transformed. Thus the energy rate is 1.313×10^7 cal./mole of reactant.

The heat of decomposition of potassium nitrate calculated from band spectra of oxygen and thermochemical data[13] is 1.03×10^5 cal./mole. Thus it seems evident that not more than 0.8% of the energy absorbed and utilized in formation of ions in the solution appears as chemical dissociation of the molecule of potassium nitrate.

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[11] Rump, *Z. Physik,* 43,254 (1937).

[12] Kulenkampff, *Ann. Physik,* **79,** 97 (1926).

[13] Villars, unpublished material.

X-Rays and Colloidal Lead

Since the discovery by Blair–Bell in England that in the treatment of cancer injection of colloidal lead followed by irradiation with x-rays materially increases the therapeutic benefits beyond those from radiation alone, there has been a great interest in the mechanism involved. There are two possibilities: that the finely divided lead produces secondary x-rays *in situ* in the tissues, or that the lead has a specific chemical effect in the tissues entirely apart from any interaction between the colloid and x-rays. In an effort to throw some light upon the mechanism, several experiments have been undertaken with colloidal lead and simple inorganic systems instead of the complex biological tissues.

Preparation of Colloidal Lead.—Solutions of colloidal lead were prepared in various dispersion media by the Bredig arc method, using pure lead electrodes of 6 mm. diameter held in an adjustable spark gap device. The beaker in which the colloid was prepared was surrounded by an ice-bath at all times. Some preparations were carried out in a nitrogen atmosphere. Much of the lead used was prepared by the following procedure. An arc was maintained for 30 minutes in 300 cc. of water redistilled from alkaline permanganate, and having a PH of 6.6 as measured by Pierre and Fudge's method. The product was centrifuged at 1200 r.p.m. for twenty-five minutes and 1600 r.p.m. for five minutes, siphoned off into containers and covered with a layer of paraffin. In some cases 0.1 cc. of 1% acetic acid was added to 30 cc. of colloidal lead before sealing.

The colloidal lead is black in thick layers and brown in thin layers or at high concentrations. It is stable for months when protected from the air but decomposes rapidly when exposed to air to form a white suspension determined by Telkes[14] as lead carbonate. It is much more stable in a nitrogen atmosphere but decomposition is not entirely prevented. Boiling does not affect the stability. Colloidal lead is coagulated by electrolytes and is a rather vigorous reducing agent. When it is placed in a U-tube fitted with electrodes the boundaries may be seen to move toward the cathode, indicating that the particles are positively charged.

TABLE II

PREPARATION OF COLLOIDAL LEAD

	Dispersion medium	Time, min.	Arc amps.	Volts	Centrifuge		Pb per 100 g. of soln.	Remarks
					Min.	R.p.m.		
1	Redist. H_2O[a]	10	2.5	40	5	840	0.04451	. .
2	Redist. H_2O	10	2.6	40	5	1200	.04451	
8	Redist. H_2O	15	2.8	40		1200	.05583	. .
						1800	.05470	b
4	Redist. H_2O	12	2.8	30–40	20	1600	. . . .	c
					5	1800	. . . .	c
6	95% Alcohol	5	2.8	35	10	1200	. . . .	d
					10	600	. . . .	d
6	10% Sucrose	10	2.8	35	20	1200	.05015	e

[a] Plus one drop of 0.1 N sodium hydroxide (PH 7). [b] Some further settling out at higher rate of centrifuging. [c] 0.1–0.2 cc. of 1% acetic acid added to tubes before sealing. [d] Coagulated. Partially settled. Some remained as colloid for over a week. [e] Less stable on standing than water solution.

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[14] Telkes, THIS JOURNAL, 49, 1382 (1927).

Table II lists the results obtained in several preparations.

The method used by Telkes for analysis was followed with slight modifications. A 25-cc. sample of colloidal lead was dissolved in 0.8 cc. of 10% acetic acid. Standard potassium dichromate was added in excess and the precipitate allowed to settle. The precipitate was then filtered off, and to the filtrate and washings were added 5 cc. of concd. hydrochloric acid and 5 cc. of 10% potassium iodide. The iodine freed was titrated after three minutes with standard thiosulfate using starch indicator.

Effect of X-Rays on the Coagulation of Colloidal Lead.—According to Crowther and Fairbrother, positive colloids are coagulated by exposure to x-rays and consequently this effect should be noted in the case of colloidal lead. A series of experiments seemed to show that the lead was not coagulated but even stabilized to a slight extent.

1. Ten cc. of colloidal lead was placed in each of two thin pyrex test-tubes and covered with a paraffin seal. One was exposed for thirty minutes at a distance of ten inches from the target of a tungsten target tube running at a voltage of 60,000 and a current of 4 to 5 amperes while the other (unexposed) was maintained at nearly the same temperature; 0.6 cc. of 2.7% calcium chloride was added to each and the tubes were viewed against a brightly illuminated background. Eight minutes elapsed before coagulation was visible in the unexposed, eleven minutes for the exposed.

2. The experiment was repeated using a 145-minute exposure at a voltage of 70,000; 0.4 cc. of 0.5% sodium chloride was added to coagulate and forty-four minutes were necessary to obtain visible coagulation of the unexposed, while fifty-three minutes were required for the exposed. This result was duplicated.

3. Two tubes of lead which had been prepared for over a month were placed in the x-ray housing, five inches from the target, one protected by a lead shield, and exposed for ten and one-half hours. A slight amount of decomposition was evident in both; 0.5 cc. of sodium chloride was added to each. In two minutes both had coagulated but the liquid in the case of the unexposed was clear, showing complete coagulation, while the other had the brown color of dilute colloidal lead, evidencing incomplete coagulation lasting for over an hour.

4. The action of rays from a molybdenum target tube operating at 30,000 volts had no apparent coagulatory effect on colloidal lead in a pyrex glass bulb 0.0035 mm. in thickness.

Secondary Radiation from Colloidal Lead.—A very thin walled pyrex tube 7 mm. in diameter and 10 mm. in length was adjusted so that a beam of x-rays from a pinhole would pass down the length without hitting the walls of the tube. Around this a piece of film was placed in a cylindrical holder of radius 2 cm. A blank taken with a ten-minute exposure of the empty tube showed no effect upon the film. The film was completely blackened in a ten-minute exposure when the tube was filled with water. With the tube filled with colloidal lead, the blackening decreased with increase in distance from the point where the beam entered the column of lead and increased with time of exposure. It is evident that the intensity of secondary rays produced from the lead when measured at a given distance from the primary beam is very much less than that for secondary rays from water under identical conditions.

Effect of Colloidal Lead upon a Chemical Reaction.—The inversion of sugar was chosen for investigation because the reaction in neutral or alkaline solution has been found to be very slightly accelerated by x-rays.

A series of experiments shows that the reaction is not appreciably affected by the presence of colloidal lead during the exposure to x-rays.

1. A 5% solution of sugar with specific rotation at 20° of 66.5 was prepared. Tests showed that the rotation was not affected by several days' standing or prolonged heating at 30°. Then 25 cc. of this solution with 2 cc. of a 0.05% solution of colloidal lead was sealed in a bulb and exposed to x-rays. A similar bulb was protected from the rays. At the end of a six-hour exposure at 60,000 volts and 2 to 5 m. a. the lead was dissolved by 0.1 cc. of *N* acetic acid and the rotation measured. The two readings checked exactly.

2. A solution of colloidal lead in sugar solution was made by arcing for five minutes in a 5% sugar solution and centrifuging for twenty minutes at 1200 r.p.m. After a four-hour exposure at 70,000 v. and 4 m. a. the saccharimeter reading of 38.3 was found to be identical for the solution containing colloidal lead and the original solution similarly exposed to x-rays.

3. Colloidal lead was prepared in a 5% sugar solution and a similar experiment carried out using an irradiation of seventeen and one-half hours. The following data were obtained.

Solution	Sacch. reading, 20°	PH
Original sugar solution	19.1	6.8
Sugar solution exposed to x-rays	19.07	6.8
Sugar soln. contg. coll. lead, 0.05 g. per 100 g. of soln.	19.15	
Sugar soln. contg. coll. lead exposed to x-rays	19.13	7.8
Sugar soln. contg. $Pb(NO_3)_2$ exposed to x-rays	18.85	5.6

Inasmuch as acetic acid had to be added to the lead in order to dissolve it, *PH* measurements could not be made. The value given was for an undissolved portion which had been exposed to the air and had formed the white cloudy lead carbonate, which did not interfere with the colorimetric measurement but showed nothing about PH of colloidal lead except that it was not acid.

It may be concluded that colloidal lead has no effect upon the inversion of sucrose by x-rays; a considerable effect is observed in the presence of lead nitrate, but the change in *PH* alone may account for this. Hence upon the basis of these experiments the mechanism of the action of colloidal lead in the tissues seems to be the specific chemical effect, rather than the production of secondary rays. This agrees with the recent observation that colloidal gold which should produce secondary rays as easily as lead, has no beneficial effects whatever in the Blair–Bell technique.

The Flocculation of Colloidal Clays

The action of x-rays in flocculating colloids is an established fact. Clay solutions are usually highly colloidal. It was the purpose of this experiment to find out the action of x-rays on the clay slips. It was taken for granted that flocculation bears a direct relationship with the viscosity of the slip, that is, flocculation increases with viscosity, other things being equal.

Advantage was taken of this relationship, therefore, by first taking a measurement of the viscosity of the slip before raying, and then after raying for a certain time. The change of viscosity is a direct measure of amount of flocculation.

The viscosity was measured by means of a viscosimeter. A certain volume of the solution was allowed to drain off continuously from a large capillary, and the time recorded accurately by means of a stop watch. The following formula expresses the relative viscosity of a slip

$$V = \frac{t_s \cdot S_s}{t_w \,.\, s_w} \,.$$

where V is relative viscosity of the slip, t_s is the time required for 100 cc. of the clay slip to flow through the viscosimeter (in seconds), S_s is the specific gravity of the clay slip, t_w is the time required for 100 cc. of distilled water at the same temperature of the slip to flow through the viscosimeter (in seconds) and s_w is the specific gravity of water at that temperature.

The clay slips were enclosed in 1-liter glass vessels tightly closed and exposed to radiation from a molybdenum target x-ray tube at 30,000 volts for 1200 milliampere hours.

The data and calculations are as follows

1. Florida Kaolin

t_s = time for 100 cc. of slip before raying to flow through the viscosimeter = 21 sec.
t_w = time for 100 cc. of water to flow through the viscosimeter = 12.0 sec.
t'_s = time for 100 cc. of slip after raying to flow through the viscosimeter = 21 sec.
$S_s = 1.210$ = specific gravity of the slip.
$s_w = 1.0$ = density of water.

Relative viscosity before raying $= \dfrac{21 \times 1.210}{12 \times 1.00} = 2.12$, the same as that after raying.

Hence x-rays have no effect of flocculation on Florida kaolin, which is a very pure kaolin.

2. Anna, Illinois, Kaolin.

t_s = 25 sec. before raying.
t'_s = 29 sec. after raying.
$S_s = 1.197$
t_w = 12 sec. $s_w = 1.0$
V before raying $= (25 \times 1.197)/(12 \times 1) = 2.49$
V after raying $= (29 \times 1.197)/(12 \times 1) = 2.90$
Increase in relative viscosity due to raying, 16.5%.

3 Tennessee Ball Clay No. 5

t_s = 22.5 sec. before raying
t'_s = 25.5 sec. after raying
$S_s = 1.200$
V before raying $= (22.5 \times 1.20)/(12 \times 1) = 2.25$
V after raying $= (25.5 \times 1.20)/(12 \times 1) = 2.55$
Increase in relative viscosity due to raying, 11.8%.

An analysis of the latter two clays shows that they are impure kaolins containing some proteins and other organic substances; the increase in relative viscosity due to raying is a relative measure of the amount of protein substance present, since the pure Florida kaolin is entirely unaffected. Therefore, the protein is most sensitive to coagulation and affects the slips markedly even though present in very small amounts.

The authors are indebted to Mr. T. Kurosawa and to Mr. D. T. Shaw for assistance in making observations, respectively on the condensation reactions and on the coagulation of colloidal clays.

Summary

1. Several chemical systems which are known to undergo photochemical change in ultraviolet light are investigated with x-rays, in most cases of an effective wave length of 0.24 Å. Most of the changes, if any, are very small.

2. The most sensitive reactions found besides oxidation of solutions of ferrous to ferric salts are a series of aldehyde-ketone condensations, investigated photochemically for the first time. Aldehyde–aldehyde condensations are much less affected by x-radiation.

3. The energy relations involved in the photolysis of potassium nitrate by x-rays are quantitatively determined, including an accurate measurement of intensity and dosage in "*r*" units with a 1 cc. air-wall ionization chamber. There are 5.58×10^{11} molecules reacting per *r* unit or approximately 0.2 molecule per ion pair. The energy in calories per mole is 1.31×10^7. Thus less than 0.8% of the energy absorbed and utilized in the formation of ions in solution appears as chemical dissociation of the potassium nitrate molecule.

4. Simultaneous irradiation of potassium iodate and potassium nitrate solutions with x-rays and ultraviolet light produces additive chemical effects in contrast with non-additive biological effects on fungi, etc.

5. A thorough test is made in potassium iodide and potassium nitrate solutions of the theory that chemical effects are secondary and due to the formation of hydrogen peroxide.

6. Colloidal lead used in the Blair–Bell technique for cancer therapy is studied from the standpoints of preparation, stability, coagulation by x-rays, production of secondary x-rays and catalytic effect in reactions subjected to irradiation. The specific chemical effect rather than the action of producing secondary x-rays in *situ* in the tissues is indicated.

7. The coagulation by x-rays as determined by viscosity changes of colloidal clay slips is found to be a function of the amount of organic protein materials present.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

THE REACTION OF IODATE AND TETRAVALENT VANADIUM IN ALKALINE SOLUTIONS

BY J. B. RAMSEY AND A. ROBINSON

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Whether or not a reaction occurs between iodate and tetravalent vanadium in alkaline solutions has apparently not been determined. That no reaction takes place in hydrochloric acid solutions of moderate concentrations (6 N or above) is evident from the results recently obtained by Swift and Hoeppel.[1] The accepted molal electrode potentials of the half-reactions involved, as given by Latimer and Hildebrand,[2] indicate that a measurable equilibrium may exist in dilute acid solutions.

The present work was initiated with the hope of making use of the reaction in alkaline solution, if such occurs, in the determination of tetravalent vanadium. The results obtained show that a reaction does take place in a conveniently short time in hot alkaline solutions, the equation of which may be written

$$6VOSO_4 + KIO_3 + 18KOH = 6KVO_3 + 6K_2SO_4 + KI + 9H_2O$$

A method of determining tetravalent vanadium by means of this reaction has been developed.

Reagents Used.—The solutions of potassium permanganate and sodium thiosulfate were prepared and standardized by the methods previously used.[3] The tetravalent vanadium solutions were prepared from ammonium metavanadate, by converting to sodium vanadate, acidifying with sulfuric acid and reducing with sulfur dioxide. After the excess sulfur dioxide had been removed by sufficient boiling in a rapid stream of air, the concentration of vanadium was determined by oxidation with a known permanganate solution.[3,4] The potassium iodate solutions were prepared from pure potassium iodate and standardized against known thiosulfate solutions. The potassium iodide was tested for iodate with negative results. All other reagents were of standard C. P. quality.

Preliminary Experiments and Results

1. Evidence of Reaction and Probable Use in Analysis.—In solutions from 0.02 to 0.2 N in alkali, nearly 0.025 *N* in tetravalent vanadium and from 0.03 to 0.05 *N* in iodate, the brown color due to tetravalent vanadium is not changed appreciably after standing for several hours at room tem-

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[1] Swift and Hoeppel, THIS JOURNAL, 51, 1366 (1929).

[2] Latimer and Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Company, New York, 1929, pp. 367 and 368.

[3] Ramsey, THIS JOURNAL, 49, 1138 (1927).

[4] Lundell and Knowles, *ibid.*, 43, 1560 (1921).

perature. (Pentavalent vanadium is colorless in alkaline solutions.) If these brown solutions are heated, they become colorless after boiling for a short time (not longer than twenty minutes in the case of any solution used). The time required is appreciably decreased by a relatively small increase in the concentration of the iodate but is not noticeably changed by a considerable change in the alkali concentration. These results indicate the possibility of determining tetravalent vanadium by oxidation with an excess of iodate in boiling alkaline solutions provided the excess iodate may be determined in the resulting solution. An obvious method of finding the quantity of excess iodate consists of adding potassium iodide, acidifying and determining the iodine formed with known thiosulfate solution.

2. Acidity Tests in Determination of Excess Iodate.—Since vanadic acid and oxygen will be present during the determinations of the excess iodate by the method proposed, it is necessary to have a concentration of acid sufficient to cause rapid reduction of iodate but not so great as to cause formation of iodine due to either the vanadic acid or oxygen during the titration with thiosulfate solution. Experiments show that if the acid concentration is 0.02 N or less in solutions containing vanadic acid, oxygen and iodide at concentrations used in obtaining the results given in the table, the quantity of iodine formed in the time required for titration is not measurable. In acidifying the alkaline iodate solution it is found that sulfuric acid having a concentration as high as 1.2 N may be used without causing the liberation of iodine by vanadic acid or oxygen due to the momentary production of high acidity. Since the volume (10 to 20 ml.) of this acid required is conveniently small, no experiments were conducted with greater acid concentration. The acid is introduced as rapidly as it will flow from a buret against the side of the reaction flask, which is kept moving in such a way as to give the solution a swirling motion.

3. Effect of Oxygen during Iodate–Vanadium Reaction.—It is well known that tetravalent vanadium is slowly oxidized by oxygen in alkaline solutions. That a large effect is produced by oxygen during the iodate–vanadium reaction is shown by the fact that if solutions of the reactants are prepared without previously excluding oxygen, as much as 20% of the tetravalent vanadium may be oxidized by the oxygen present. Results given in the table show the effect of oxygen present in the vanadium solution alone.

4. Catalysis of the Iodate–Vanadium Reaction.—Failure to remove the dissolved oxygen completely in the earlier attempts gave results which were then assumed to be due to the incompleteness of the reaction. Various substances were introduced which might remove the vanadate more completely from the assumed equilibrium. None of the substances tried eliminated the error. However, disodium acid phosphate, one of those used, was found to catalyze the reaction appreciably. With phosphate present, the solution became colorless after boiling four or five minutes while without it, ten to twelve minutes were required in solutions otherwise the same. At present we are unable to give a probable explanation of this catalytic effect.

General Analytical Procedure

On the basis of these experiments, the following procedure is the one finally adopted. Measured volumes of known solutions of alkali, iodate and phosphate are mixed in a 400-ml. Florence flask. The resulting solution is boiled for about four minutes to remove oxygen. During this time a measured volume of acid vanadyl sulfate solution is treated for removal of oxygen in one of two ways, either by boiling or by addition, in the cold, of a small volume of saturated sodium bicarbonate solution. About five minutes after adding the bicarbonate, the vanadium solution is added dropwise from a dropping funnel to the boiling iodate solution. When the vanadium solution is boiled to remove the oxygen, it is added while still hot to the boiling iodate solution. After the reaction is completed, as shown by the disappearance of the brown color, the solution is cooled in tap water and diluted to approximately 250 ml. About two grams of potassium iodide is then added and the solution is acidified. To determine the quantity of acid needed, one run is made in which the acid is added slowly until iodine is formed. Starch solution is added and the iodine reduced carefully with thiosulfate. With addition of more acid, iodine is liberated and again reduced. This is continued until no iodine is formed on addition of more acid. The last portion of acid is added dropwise. The quantity of acid found necessary is introduced in all other runs in the manner previously described. The titration with thiosulfate solution is made immediately after acidification. The starch solution is added after almost all of the iodine has been reduced.

Results

In obtaining the results given in the following table, the volumes and approximate concentrations of the solutions used were as follows: 50 ml.

TABLE I

OXIDATION OF TETRAVALENT VANADIUM BY IODATE IN ALKALINE SOLUTION

Expt.	Vanadium taken, millieq.	Iodate reduced, millieq.	Diff., millieq.	Treatment of vanadium solution
1	2.027	2.033	+0.006	Boiled for three to five minutes
2	2.027	2.027	.000	
3	2.027	2.031	+ .004	
4	2.027	2.026	− .001	
5	2.027	2.028	+ .001	
6	2.027	2.028	+ .001	
7	2.027	2.025	− .002	
8	2.027	2.009	− .018	Oxygen not removed
9	2.027	2.001	− .026	
10	2.990	2.989	− .001	Treated with sodium bicarbonate solution
11	2.990	2.986	− .004	
12	2.990	2.988	− .002	
13	2.990	2.991	+ .001	
14	2.990	2.986	− .004	
15	2.990	2.986	− .004	
16	2.990	2.987	− .003	

of standard potassium iodate solution (approximately 0.1 *N*); such a volume (between 10 and 20 ml.) of approximately 4.0 *N* potassium hydroxide that the solution remains alkaline after completion of the reaction; 10 ml. of approximately 0.25 F disodium hydrogen phosphate; 25 ml. of standard vanadyl sulfate solution, approximately 0.1 *N* in vanadium and 1.5 *N* in sulfuric acid; the required volume of approximately 1.2 N sulfuric acid, which is usually between 10 and 20 ml. The volume of standard thiosulfate solution (approximately 0.1 *N*) is in every case between 20 and 30 ml.

From the results of Expts. 8 and 9 it is seen that, on the average, approximately 1% of the tetravalent vanadium used is oxidized by the oxygen present in the vanadium solution alone. If oxygen is excluded from all solutions, the results obtained are, on the average, within 0.1% of those calculated.

Summary

It has been shown that iodate and tetravalent vanadium react completely in hot alkaline solutions. Phosphate has been found to catalyze this reaction.

A method of determining vanadium by means of this reaction has been described. The results check on the average within 0.1% of the calculated if oxygen is excluded during the reaction.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY, MCGILL UNIVERSITY]

THE DIELECTRIC CONSTANTS OF WATER AT VARIOUS TEMPERATURES

BY A. C. CUTHBERTSON AND O. MAASS

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As a step in the measurement of the dielectric constant of hydrogen peroxide it was found necessary to use water for purposes of comparison. A large divergence exists in the values of the dielectric constant given for water and little attention has been paid to the measurement of the temperature coefficient over a wide range. This led to the development of the method described below in which measurements were carried out between 0 and 75°. This method offers no originality in its main principles but in the details of procedure improvements have been made which lead to consistent results.

Experimental

General Outline.—The method employed involves the resonance principle for the measurement of capacity in the ingenious set-up described by Williams and Krchma.[1] The distinguishing feature from that used

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[1] Williams and Krchma, THIS JOURNAL, 48,1892 (1926).

by them lies principally in the design of the dielectric cell and the insertion of an invariable capacity in series with the dielectric cell and tuning condenser.

A diagram of the apparatus is shown in Fig. 1. As the source of oscillations two Hartley oscillators were employed designated as A and B in the figure. The inductances in both cases consisted of 75-turn honeycomb coils. A tap taken off at 50 turns was connected to the filament lead of the vacuum tube. In the case of A the inductance was shunted by a General Radio Condenser of the type used in wavemeters. In order to increase the accuracy of the readings a mirror was mounted vertically at the center of the dial so that the scale readings could be read by reflected light on a circular millimeter scale 4 feet in diameter. This type of condenser was supplied with a vernier control. The small composition knob was removed and a 1-inch brass pulley substituted. By means of a cord belt and another pulley 5 feet distant it was possible to tune the condenser without being sufficiently close to introduce body capacity effects. In the plate circuit a choke coil F was inserted to act as an impedance, which prevented radio frequency currents from passing through the plate circuit.

The fixed oscillator B was shunted with a variable condenser whose capacity could be varied to suit the measurement, but it was of course fixed at a definite value for any one. The telephones G used to indicate the point of resonance between the two circuits occupy the same position in B that the impedance F does in A.

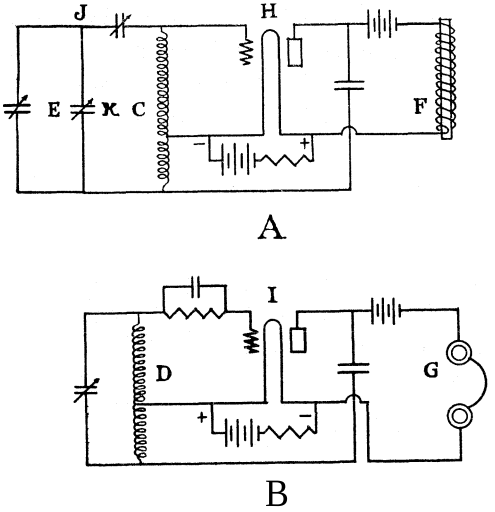

Fig. 1.—A, Variable oscillator; H, 171A. radiotron; F, impedance coil; C, inductance; J, series condenser; K, tuning condenser; E, dielectric cell; B, fixed oscillator; I, U. v. 199 Radiotron; G, phones; D, inductance.

A 171A Radiotron tube was found satisfactory for the circuit in which the dielectric cell was connected, *i. e.*, A. In this circuit the oscillations have to be forced through substances which have a measurable conductivity and which show a tendency to absorb, and therefore it was necessary to place a capacity J in series with the variable tuning condenser and dielectric cell. Measurements could be made up to a conductivity of 10^{-5}. In the fixed oscillator B a U. v. 199 Radiotron was used.

Dielectric Cell.—The success of the method was found to depend very largely on the construction of the dielectric cell. The ordinary type of two fixed plates has disadvantages, one of the most important being "capacity lead effects." The one to be described was constructed on the principle of a variable condenser the plates of which could be immersed in the liquid. The container of the liquid acted as a support for the cell. It consisted of two sets of semicircular plates. One set was fixed and may be designated as the stator plates. These were bolted by means of brass rods to an insulating frame of hard rubber. The other set, known as the rotor, was fitted to a brass axle. The vertical position of the axle was so adjusted that the rotor plates would mesh with the stator plates. In order to fix rigidly the position of the two sets, the axle supporting the rotor one passed through two bearings, one through the insulating Frame, the other a short distance above the plates. The latter was attached to but insulated from the brass rods supporting the stator plates, A vernier dial was fixed by means of a set screw to the brass axle and bolted by two screws to the same frame which supported the stator plates. This dial served to hold the rotor plates in position and also provided a means of setting the plates to a given capacity value. The liquid to be measured was placed in the container and the plates of the cell were immersed in it. A lid fastened to the insulating frame held it in position.

This type of cell removed any capacity lead effects. In actual use it was permanently connected in the circuit and set at a definite capacity value as given by the dial reading. Tuning of the variable condenser to which it was connected in parallel brought the oscillator A to resonance with B and the scale reading was noted. Readings were taken at two resonance positions of the variable condenser, first when the cell was filled with air, or a substance of known dielectric constant, second with the substance whose value was to be determined. The ratio of the differences in readings on the tuning condenser gives the ratio of the dielectric constants. This eliminates the end effects in the condenser, provided that the capacity setting is neither too small nor too large. Under these conditions the capacity varies in a linear way.

The dielectric constants of various substances vary from about unity to one hundred. It is not always practical to compare the liquid in question to air. The reason for this is that either the accuracy in the determination of air or the substance possessing a large dielectric would have to be sacrificed. With water as the dielectric the capacity of the cell is approximately 80 times that when air is present. If a large enough capacity were used to give a large scale reading for air then, using the same tuning condenser, the capacity of the same cell with water would be too large to measure.

In order to avoid sacrificing the accuracy of the air or water measurement, a "step-by-step" method was adopted. The flexibility in design of the cell permitted this to be accomplished easily. The stator plates were held in position by means of nuts threaded to the supporting brass rods. Separation was accomplished with machined brass washers. The capacity of such a condenser could be altered in one or both of two ways. In the first place the stator plate separation could be increased or decreased by a thickness of one or more washers. A corresponding alteration was of course made in the rotor plates. En the second place the number of stator and rotor plates could be increased or decreased, *i. e.*, a 3, 5, 7, 9, etc., plate condenser was readily constructed, depending on the magnitude of the constant to be measured.

The scheme is exemplified in the following way. A 9-plate condenser made possible an accurate determination of chlorobenzene relative to air. A 5-plate condenser allowed a comparison to be made between chlorobenzene and nitrobenzene, while 3 plates served to establish the relationship between nitrobenzene and water. The vernier dial was divided into 100 divisions corresponding to 180°. Instead of merely taking a reading at 20 and re-setting the dial at 80, resonance points were obtained at 20, 30, 40, 50, 60, 70 and 80—or whatever range was most convenient. In order to illustrate the experimental procedure, results are given for this particular series and are tabulated in Table I and plotted in Fig. 2.

Results

Curves 1 and 2 represent the relative capacity of air and chlorobenzene using a 9-plate condenser; 3 and 4 that of chlorobenzene and nitrobenzene with a 5-plate condenser, while 5 and 6 represent the relationship between nitrobenzene and water, the comparison being made in a 3-plate condenser.

The values of the dielectric constants can be computed easily from the

Table I

Resonance Readings for Various Settings of Dielectric Cell. Temperature, 25°

Cell settings	Readings at resonance	Cell settings	Readings at resonance	Cell settings	Readings at resonance
Air, 9-plate condenser		C_6H_5Cl, 9-plate condenser		C_6H_5Cl, 5-plate condenser	
20	5.90	20	11.50	20	5.20
30	6.80	30	16.30	30	7.50
40	7.70	40	21.60	40	10.30
50	8.60	50	26.80	50	12.80
60	9.50	60	31.30	60	15.30
70	10.40	70	36.60	70	17.90
80	11.30	80	41.30	80	20.45
$C_6H_5NO_2$, 5-plate condenser		$C_6H_5NO_2$, 3-plate condenser		Water, 3-plate condenser	
20	11.25	20	3.10	20	11.50
25	19.50	30	7.50	25	16.55
30	27.70	40	12.10	30	21.35
35	35.50	50	16.70	35	26.40
40	43.15	60	21.60	40	31.40
		70	26.30	45	36.50
		80	30.70	50	42.00
				55	46.90

above data as in every case they are inversely proportional to the slope of the line which is obtained by plotting the setting of the condenser against the capacity. As a result the dielectric constants for chlorobenzene, nitrobenzene and water based on air as unity are found to be 5.61, 35.20 and 75.40, respectively.

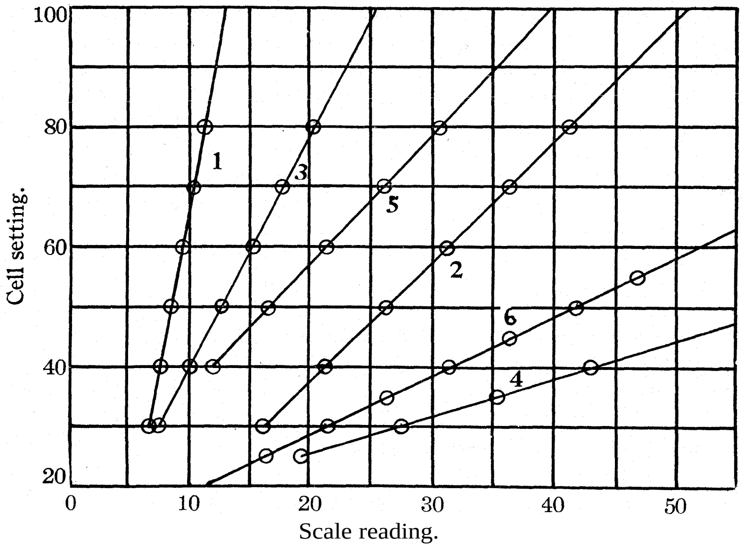

Fig. 2.

In order to check the value for water a 5-plate condenser made possible a comparison between air and ether, a 3-plate between ether and water. The results gave 4.02 and 75.5 as the dielectric constants of ether and of water at 25°.

A direct comparison was made for benzene. The value obtained was 2.28. All substances mentioned above had been carefully purified by standard methods. It may be pointed out that the value obtained for water will be independent of the purity of the substances used in the intermediate steps.

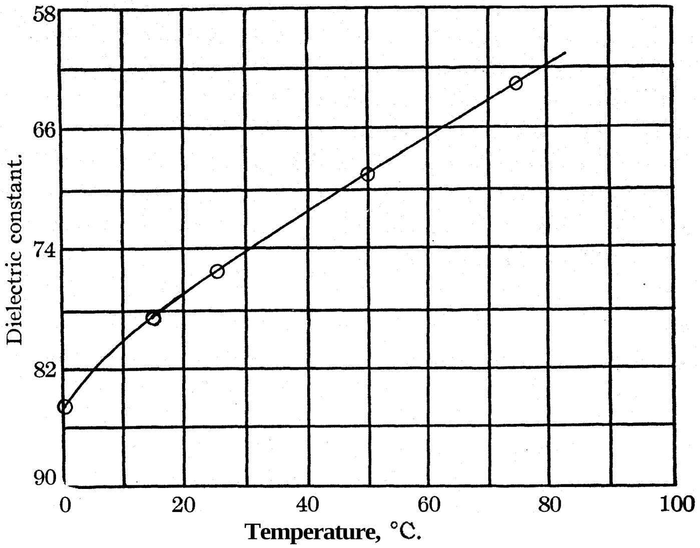

Fig. 3.

The Temperature Coefficient of Water.—From the above results the dielectric constant of water at 25° is 75.4. The effect of temperature was then investigated over the range 0 to 75°. Using the same 3-plate condenser which gave the value for water at 25°, the others were obtained at 0, 15, 50 and 75°. The values obtained at 0, 15, 50 and 75° were 84.4, 78.5, 69 and 62.9, respectively, all based on the value 75.4 at 25°. The above values were obtained repeatedly; especially the one at 0° was measured often. The values checked with one another within 1%, of which the above values are the mean.

The relationship between the dielectric constant and temperature is shown in Fig. **3.**

Discussion of Results

From 25 to 75° the relationship between the dielectric constant of water and temperature is approximately linear, the temperature coefficient being -0.258. From 0 to 15° the average value is -0.390, while the intermediate value between 15 and 25° is −0.310. The temperature coefficients[2] over a narrow range found by various observers vary from −0.28 per °C. to −0.495; the lowest value, −0.28, obtained by Nernst[3] is in best agreement with the value obtained by the authors

The most thorough investigation of the temperature coefficient of the dielectric constant is that carried out after the above compilation was made by Lattey. L. Kockel[4] made measurements over the range 0 to 100°. The resonance method with the particular set-up used did not give results on account of the conductivity of the water. The Nernst bridge method was then resorted to and the results were based on the absolute value of the dielectric constant of toluene. At 50° the value obtained by L. Kockel agrees with that of the authors, below the values are greater and above less. At 0° the difference amounts to 4%. The average temperature coefficient over the range 0 to 15° is 0.30 as compared to 0.35 above.

As to the value of the dielectric constant at 18°, the mean of the values obtained by various observers is S1.05, while that of the authors is 77.0 (the wave length used was 200 meters).[2]

The dielectric constants of benzene, chlorobenzene and nitrobenzene check well, however, with the accepted values. That of Isnardi,[5] 2.273, is usually taken as standard, so that the value 2.28 is probably accurate to 0.5 of 1%. In the case of chlorobenzene the constant 10.95 of Veley in Landolt-Börnstein's Tables is in error, as pointed out by Williams and Krchma[1] and Smyth, Morgan and Boyce.[6] The value 5.61 is in good agreement with their values. For nitrobenzene the values in Landolt-Börnstein's Tables are reasonably close to 35.2.

The Polarizability of Water at Various Temperatures.—The molecular polarizability P of a substance is given by

$$P = \frac{E-1}{E+2}\cdot\frac{M}{d}$$

E = dielectric constant
M = molecular weight
d = density

The values of P at various temperatures were calculated and the results tabulated in Table II.

TABLE II

POLARIZABILITY OF WATER

Temperature, °C.	0	15	25	50	75
Polariz., $(E-1)/(E-2)\cdot M/d$	17.38	17.35	17.36	17.45	17.62

For a substance having a large dielectric constant, the polarizability will vary less with the temperature than for a substance having a small one. Consequently, when the dielectric constant reaches a large value,

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[2] Lattey, *Phil. Mag.*, *41*, *829 (1921).*

[3] Nernst, *Z. physik. Chem.*, *14*, *622 (1894).*

[4] Kockel, *Ann. Physik*, **77A,** *417 (1925).*

[5] Isnardi, *Z. Physik*, 9, **153** *(1922).*

[6] Smyth, Morgan and Boyce, THIS JOURNAL, 50, 1536 *(1928).*

m

as is the case in water, variation in density will largely govern the variation in the polarizability. Furthermore, water in the liquid state is a substance in which the molecules show a great tendency toward association, which doubtless varies with the temperature. The Debye equation which would apply when the molecules are free to assume a random orientation, has no significance for a substance of this kind. An attempted calculation of the electric moment only serves to make this evident.

Any significance which may be attached to the above values is best left until more data are obtained.

Acknowledgment is made to the National Research Council of Canada for a bursary and studentship held by one of us, during the tenure of which the above work was carried out.

Summary

A resonance method for the measurements of the dielectric constant of pure liquids is described, involving the use of a variable dielectric cell in which lead and end effects are eliminated and the dimensions of which can be altered over wide limits.

The dielectric constants of ether, benzene, chlorobenzene and nitrobenzene were measured at 25°. The dielectric constant of water was determined between 0 and 75°. The step-by-step method used made it possible to make absolute determinations based on air as unity.

The polarizability of water was calculated from the dielectric constant data. The futility of applying the Debye equation for this substance was pointed out.

MONTREAL, CANADA

[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY, MCGILL UNIVERSITY]

HYDROGEN PEROXIDE. VII. THE DIELECTRIC CONSTANTS, REFRACTIVE INDICES AND IONIZING POWER OF HYDROGEN PEROXIDE AND ITS AQUEOUS SOLUTIONS

BY A. C. CUTHBERTSON AND O. MAASS

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Dielectric Constants.—The measurements referred to in the title may most conveniently be taken up in separate sections.

The determination of the dielectric constants of hydrogen peroxide and its aqueous solutions presents two difficulties: the tendency of the peroxide to decompose and conduction of the solutions due to impurities. The first of these was very largely overcome by constructing a cell similar to the one described elsewhere[1] but made of tin. The second difficulty was eliminated by paying particular attention to the purification of the peroxide. It was found that of all metals very pure tin showed the least

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[1] Cuthbertson and Maass, THIS JOURNAL, 52,483 (1930).

catalytic effect in causing decomposition. Every part of the condenser which had contact with the peroxide was therefore made from tin. The stator plates of the three-plate condenser were tin soldered to two tin tubes which were reinforced by inner brass rods, the upper ends of which were tightly clamped to a plate of bakelite. The center of the rotor plate was similarly fastened to a rod which passed through a bushing and then fastened to a vernier dial. This ensured the necessary rigidity and reproducibility in the setting of the cell. All the measurements were carried out at zero in order to minimize decomposition, which after a long immersion made itself evident by the formation of small bubbles of oxygen on the plates of the condenser.

The peroxide used was distilled from alkaline solution and subsequently recrystallized after concentration. The aqueous solutions were obtained by diluting with distilled water. It might be mentioned in this connection that conductivities higher than 10^{-5} made measurements difficult. In order to indicate the reproducibility and accuracy of the results the experimental data are given in Table I. The calculations of the dielectric constants are based on 84.4 for water at 0°. The relationship between percentage of hydrogen peroxide and dielectric constant is shown in Fig. 1.

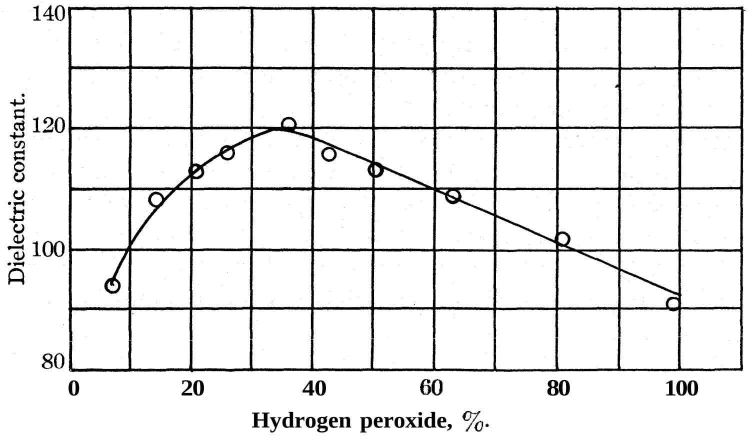

Fig. 1.

It will be noticed that the calibration value for water remains constant in a series of readings but varies a little from one series to another for the same cell setting. This was due to permanent changes on the handling of the cell between runs and does not enter into the results as calculated for any one series. After each peroxide measurement a water determination was made.

Observation showed that only very slight decomposition occurred, so that after a five-minute interval no appreciable change could be detected. After standing for a period of two hours, however, the relative

TABLE I

Capacity Values for Hydrogen Peroxide and its Aqueous Solutions Relative to Water at 0°

H_2O_2, %, 99.45
Cell setting 80-20

Relative capacity	Water value
33.20	31.30
33.20	31.50
33.30	31.40
33.20	31.70
33.30	31.60
33.50	31.50
33.10	
33.30	
33.30	
Av. 33.28	31.50

Dielectric constant, 89.2

H_2O_2, %, 98.87
Cell setting 80-20

Relative capacity	Water value
34.85	32.10
34.70	32.05
34.65	32.30
34.65	32.10
	32.10
Av. 34.71	32.11

Dielectric constant, 91.2

H_2O_2, %, 81.27
Cell setting 80–20

Relative capacity	Water value
38.85	
38.50	
38.60	
38.75	
38.80	
38.90	
Av. 38.67	32.11

Dielectric constant, 101.6

H_2O_2, %, 63.8
Cell setting 80–20

41.50	
41.40	
41.30	
41.35	
Av. 41.39	32.11

Dielectric constant, 108.8

H_2O_2, %, 50.23
Cell setting 80–20

43.20	31.70
43.25	31.60
43.35	31.90
43.20	31.80
43.20	31.60
	31.70
Av. 43.24	31.71

Dielectric constant, 115.0

H_2O_2, %, 43.25
Cell setting 60–20

31.20	22.20
31.0	22.40
31.1	22.40
30.8	22.20
31.70	22.20
31.3	
Av. 31.0	22.32

Dielectric constant, 116.2

H_2O_2, %, 36.3
Cell setting 60–20

31.80	
31.80	
31.80	22.32
Av. 31.80	22.32

Dielectric constant, 121.1

H_2O_2, %, 32.0
Cell setting 60-20

31.70	
31.70	
31.50	
31.30	
31.50	22.32
Av. 31.54	22.32

Dielectric constant, 119.0

H_2O_2, %, 25.8
Cell setting 60–20

30.70	
30.70	
30.60	22.32
Av. 30.67	22.32

Dielectric constant, 116.0

H_2O_2, %, 20.8
Cell setting 60-20

30.00	
29.70	
30.30	22.32
Av. 30.00	22.32

Dielectric constant, 113.5

H_2O_2, %, 14.0
Cell setting 80–20

43.40	33.80
43.00	33.70
43.70	33.70
43.50	33.60
43.50	33.60
Av. 43.42	33.62

Dielectric constant, 108.5

H_2O_2, %, 6.9
Cell setting 80–20

37.70	
37.20	
37.40	33.62
Av. 37.40	**33.62**

Dielectric constant, 94.0

capacity was measurably lowered due to the formation of bubbles, although the extent of the decomposition could not be detected analytically. All the measurements tabulated above were made before the capacity was altered by bubble formation.

The occurrence of a maximum in the curve relating the dielectric constant and percentage hydrogen peroxide was not anticipated. The phenomenon has, however, been observed before. Partington[2] showed that a maximum exists in the binary mixture benzoic acid and benzene. It is known that peroxide and water form a complex but whether this exists at so high a temperature as 0° and at the same time is responsible for the maximum is problematical. The maximum occurs at **35%** hydrogen peroxide and this does not correspond with the composition of the molecular compound.[3] This fact however does not prove that the latter has no influence on the constant. The fact that the complex is bound to be dissociated and the hydrogen peroxide with its higher dielectric constant might have less influence on the slope of the curve.

The dielectric constant of pure hydrogen peroxide is 89.2 at 0°, based on a value of 84.4 for water. There is a reference in the literature to a value obtained by Calvert[4] of 84.7 for a 45.9% solution at 18°. This value has been extrapolated for the 100% solution. Measurements at temperatures other than 0° will be attempted in the near future.

Refractive Indices.—The measurements were carried out with a goniometer using the method described previously.[5] A hydrogen tube was used and the refractive indices were measured by means of the three lines 6563, 4861 and 4340. The values are given in Table II.

TABLE II

REFRACTIVE INDICES 24.5°

H_2O_2, %	H lines 6563	4861	4340
13.85	1.3409	1.3476	1.3515
35.48	1.3557	1.3623	1.3657
55.60	1.3701	1.3768	1.3814
74.79	1.3851	1.3914	1.3984
89.36	13.957	1.4032	1.4091

The above values were plotted against concentration of hydrogen peroxide and the refractive indices of 20, **35,** 40, 60, 80 and 100% hydrogen peroxide were taken. n_∞ was obtained for the above concentrations by extrapolation by means of the Cauchy Formula and MR_∞ was calculated.

The curves relating refractive index to concentration show no abnormalities as observed in the dielectric constant determination. The same

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[2] Partington, *Phil.* Mag., [7] 1, 1035 (1926).

[3] Maass and Herzberg, THIS JOURNAL, 42, 2569 (1920).

[4] Landolt–Bornstein, "Tabellen."

[5] Maass and Hatcher, THIS JOURNAL, 42, 2548 (1920).

TABLE III

REFRACTIVE POWERS AND POLARIZABILITY

H_2O_2 %	n_α	MR_α	Polarizability
0	1.3239	3.610	17.38
20	1.3360	3.854	18.01
35	1.3460	4.110	18.50
40	1.3495	4.154	18.70
60	1.3637	4.533	19.55
80	1.3756	4.964	20.71
100	1.3910	5.643	22.52

holds true for n_α plotted against concentration. All the values fall approximately on continuous gentle sloping lines and the largest deviation occurs in the case of the blue line for H_2, viz., 4340. This is undoubtedly due to the experimental error because the blue image was not as well defined as the other two and therefore increased somewhat the difficulty of focusing the cross hairs of the telescope on it.

Maass and Hatcher[6] obtained 1.4140 for the refractive index of pure peroxide for the sodium D line and 1.4043 at 96.81%. From the values given the latter is in good agreement but the first is too high. On recalculating the value for pure peroxide from the prism and angle of minimum deviation in their paper an arithmetical error was found. Recalculation gave 1.4063, in agreement with the above results.

The change in the value as originally published is too slight to affect the argument relating MR_D and constitution. The value of the molecular refractive power 5.805 is too large for two hydroxyl oxygens and too small for a quadrivalent oxygen if the value found by Miss Homfray[7] in pyrone salts be accepted. The dispersive power also gives values for hydrogen peroxide not truly additive on the basis of hydroxyl oxygens. The dispersive power between the H lines—6563 and 4340—equals 0.410. The atomic dispersions for the same lines amount to 0.036 and 0.019 for hydrogen and hydroxyl oxygen, respectively. This gives a calculated value of 0.110 compared to an observed of 0.410.

Neither the refractive power nor dispersive power of hydrogen peroxide appears to offer decisive proof as to the correct formula for this substance. Some evidence of value may, however, be obtained by a consideration of Sugden's[8] parachor. On the basis of the following formulas the calculated values of the parachor are given.

Formula	HO—OH	H—O—H O	H—O ⟶ O H
Parachor calcd.	74.1	97.7	72.5
Parachor obs.	69.6	..	..

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[6] Maass and Hatcher, THIS JOURNAL, 42, 2548 (1920).

[7] Homfray, J. Chem. *Soc.*, 87, 1443 (1905).

[8] Sugden, *ibid*., 125, 1185 (1924); *ibid*., 127, 1525 (1925).

The calculated value for the parachor corresponding to (3) most nearly approaches the observed value of 69.6. This formula represents what is termed a coordinate link, *i. e.*, the electrons shared by the two oxygen atoms come from the oxygen atom attached to the two hydrogen atoms.

It appears reasonable then to suppose that the calculated values of the molecular refractive and dispersive power of hydrogen peroxide would agree, were the atomic refractive power of a coordinate linked oxygen atom known. On the basis then of the deviation shown in all three cases for Formulas 1 and 2, 3 is to be taken as correct, and the atomic refractive power of a coordinate oxygen linked to another is 2.1.

The electric moments calculated by the Debye equation for aqueous solutions of hydrogen peroxide of various strengths were all found to have approximately the same value. This value has no significance in view of the fact that one is dealing with a binary mixture both the components of which are highly associated. The interest of such a calculation lies in that it makes evident that even if a maximum occurs in the dielectric constant no such maximum need be expected in n_∞. The polarizability is given by $\frac{E-1}{E+2}\cdot\frac{M}{d}$, where M is calculated on the basis of molar fractions and, although E passes through a maximum on varying the concentration of peroxide, the polarizability increases continuously when E is large.

Ionizing Power.—In measuring the conductivity of solutions in which peroxide is the solvent, care must be taken to avoid decomposition at the electrodes. Tin has proved to be the most suitable metal and to avoid polarization a method was employed the principle of which is described by Bouty[9] and Sheldon.[10] In outline the apparatus used in this investigation consisted of a glass cell into which four tin electrodes could be inserted. A current of less than 0.001 ampere was passed through the solution, the circuit being made through the two outer electrodes, which may be termed the primary ones. A quadrant electrometer connected to the other two (secondary electrodes) made possible the measurement of the potential difference between two fixed points in the solution. By means of a double throw switch connected to the electrometer and across a resistance box which is in series in the primary circuit, it was possible to measure the drop of potential across both the fixed electrodes and the known resistance. The ratio of the quadrant electrometer readings in the two cases made possible the calculation of the resistance of the solution in question since the same current is flowing through both.

Figure 2 gives a diagrammatic sketch of the cell in the form of a U-tube with two other glass tubes sealed into the horizontal portion and in

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[9] Bouty, *J. de phys.*, 3, 325 (1884).

[10] Sheldon, *Ann. Physik*, 34, 122 (1888).

the same plane as the two outer arms. In the outer arms the primary electrodes were inserted while the drop of potential was measured across the two inner ones by means of the electrometer. The current was supplied by a number of dry cells and passed through the resistance box R and solution on closing the switch S. The double switch K made possible the quick comparison of the potential drop across E, E or R.

Owing to the irregularities in the semi-circular scale and the position of the electrometer relative to it, the scale deflections were not exactly proportional to the potential differences measured. The following method of correction was applied. Three dry cells were used. Each in turn was connected across the quadrants of the electrometer and the deflection determined in all three cases. Two were then connected in series and finally the deflection was noted for all three in series. A graph of the necessary correction for any deflection was then used.

The method used in the determination of the cell constant will illustrate the general method employed in the conductivity measurements. A solution of $N/10$ potassium chloride was poured into the cell and the four tin electrodes were placed in position. The two outer electrodes were connected in the circuit of the cell C and the resistance R. R had in this case a value of 22,000 ohms. The secondary electrodes were connected to one pair of end terminals of the double throw switch K while the other two shunted the resistance R. One of the center terminals was connected to ground, the other to one pair of quadrants. The other pair of quadrants was grounded. The switch K was thrown in turn across the secondary electrodes E, E and the resistance R and the corrected scale readings 4.02 and 13.65 were obtained. Hence the resistance of the cell was $(4.02/13.65) \times 22{,}000 = 6471$ ohms, and the cell constant k becomes $= 6471 \times 1.17 \times 10^{-2} = 75.82$, where 1.17×10^{-2} is the specific conductivity of a $N/10$ potassium chloride solution at 20°. The solution in the cell was then replaced by a $N/100$ potassium chloride solution and deflections of 15.42 and 5.72 were obtained for the secondary electrodes and resistance. Hence the specific conductivity of this solution is

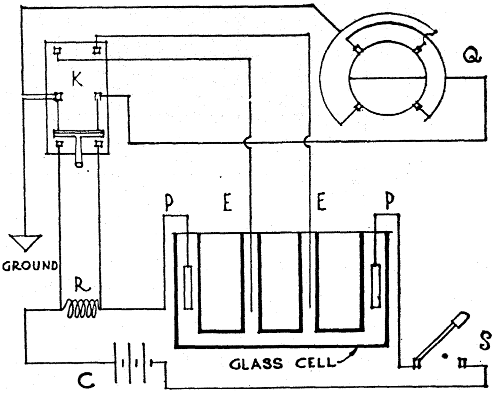

Fig. 2.

$$(75.82) \div \left(\frac{15.42}{5.72} \times 22{,}000\right) = 1.278 \times 10^{-3}$$

which is in agreement with the established value.

It might be mentioned here that in a series of measurements involving the same cell and electrodes, any change in the position of the secondary electrodes was obviated by having the electrodes of such a length that they did not reach the main body of the liquid in the horizontal portion of the cell,

Varying the position of the primary electrodes between measurements makes no difference in the ratio of the deflections.

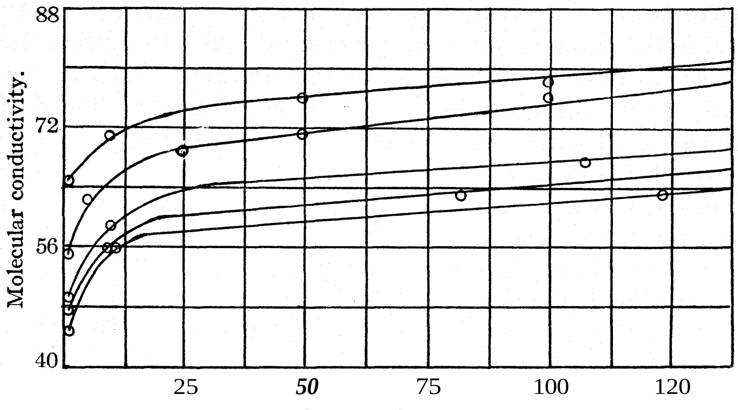

Fig. 3.

By varying the cross section of glass connection several cells were made having widely different constants and these cells were used according to the resistance of the solution. As a source of current dry cells up to **30** volts were employed and their number and the resistance up to 100,000 ohms chosen in such a way that deflections of proper magnitude were obtained. With the small currents used, no variation in the current could be detected during long periods. In any case the measurements as carried out are quite independent of the current, provided it does not change during the short interval required to measure the two deflections.

Excellent results were obtained by means of the above method. Especially noticeable was the accuracy with which solutions having a very low conductivity could be measured.

The specific conductivity of freshly crystallized peroxide was found to be of the order 2×10^{-6}. This must be taken as the upper limit since the crystallization and measurements were carried out in glass vessels. This conductivity would correspond to a hydrogen-ion concentration of 4×10^{-6} or less than one-tenth of that given by boric or carbonic acids but fifty times as great as pure water. If therefore hydrogen peroxide is an acid it is an exceedingly weak one. On diluting the peroxide the concentration of some of the solutions was found to increase if they were allowed to stand in glass vessels.

In the case of solutions of low conductivity, for which the results are given below, the conduction of the solvent was determined so that proper corrections could be applied. This was only necessary in the case of the acetic acid solutions and very dilute potassium chloride solutions.

Table IV

Conductivity of Potassium Chloride in Hydrogen Peroxide and its Aqueous Solutions at 0°

H_2O_2, %	Dilution in liters	Spec. cond.	Mol. cond
22.26	0.500	9.62×10^{-2}	48.1
	1.020	5.36×10^{-2}	54.7
	5.00	1.26×10^{-2}	62.8
	25.0	2.64×10^{-3}	69.5
	50.0	1.41×10^{-3}	70.5
	100.0	7.63×10^{-4}	76.3
35.48	1.10	4.84×10^{-2}	53.3
	10.10	5.88×10^{-3}	59.3
	107.3	6.30×10^{-4}	67.5
90.2	1.016	5.00×10^{-2}	50.8
	9.083	6.15×10^{-3}	55.9
	82.10	7.73×10^{-4}	63.2
100	0.995	4.51×10^{-2}	44.8
	11.1	5.11×10^{-3}	56.3
	123.0	6.12×10^{-4}	63.0

The following results were obtained for acetic acid at 0°.

Table V

Conductivity of Acetic Acid in Aqueous Hydrogen Peroxide Solutions at 0°

H_2O_2, %	Dilution in liters	Spec. cond.	Mol. cond.
22.26	0.486	6.44×10^{-4}	0.315
	1.200	5.01×10^{-4}	.757
	12.00	1.74×10^{-4}	2.090
	60.00	7.34×10^{-5}	4.40
	120.0	5.12×10^{-5}	6.14
	600.0	2.09×10^{-5}	12.5
	1200.0	1.69×10^{-5}	20.3
90.2	0.901	2.22×10^{-5}	0.020
	5.64	1.01×10^{-5}	.057
	273.0	6.1×10^{-6}	1.66

Probably the most satisfactory method of discussing the conductivities of potassium chloride and acetic acid in aqueous solutions of hydrogen peroxide is to compare them with those of water. For this purpose a series of curves is included to show the relation between the molecular conductivity and dilution for potassium chloride. The curves for water and 22.26, 35.48, 90.2 and 100% H_2O_2 are all of the same type as water. Further, as the percentage of H_2O_2 increases, the molecular conductivity for any one dilution decreases regularly. It might have been expected that the 35.47% H_2O_2 solution would show abnormalities comparable with the dielectric constant. Such, however, does not appear to be the case. From the fact also that the dielectric constant of all the solutions is higher than in the case of water, it would be anticipated that all of the solutions would show a higher value than water with respect to specific or molecular conductivity.

The ionizing power, however, with which the value of the dielectric constant is presumably most directly connected, is best investigated by determining the ratio of the molecular conductivity at any dilution with that at infinite dilution. To calculate accurately by extrapolation methods the molecular conductivity at infinite dilution necessitates the specific conductivities of solutions of from $N/1000$ to $N/10{,}000$. Such data are not available from the present measurements. In order to approximate this value for the various solutions, the following method was resorted to. The molecular conductivities were plotted against percentage of peroxide for dilutions of 10, 20, 40 and 100.

The value of the molecular conductivity of potassium chloride in water was taken as 81.5 at infinite dilution and 0° and the curve was drawn, by proportionality considerations, to those obtained at dilutions of 10, 20, 40 and 100. In this way then an approximation to the conductivities at infinite dilution was made, and was for 100% H_2O_2, 65.5; 90% H_2O_2, 66.0; 35.5% H_2O_2, 71.5; 22.2% H_2O_2, 75.8. A comparison can now be made for the apparent dissociation of potassium chloride in water and in the peroxide solutions.

TABLE VI

COMPARISON OF POTASSIUM CHLORIDE DISSOCIATION IN WATER AND IN HYDROGEN PEROXIDE SOLUTIONS AT VARIOUS DILUTIONS

H_2O_2, %	Dissociation	H_2O_2, %	Dissociation	H_2O_2, %	Dissociation
Dilution 10		Dilution 50		Dilution 100	
100	0 848	100	0.945	100	0 957
90	.856	90	.952	90	.962
35.5	.830	35.5	.928	35.5	.942
22 2	.868	22.2	.941	22 2	.971
Water	.877	Water	.932	Water	.955

The approximate ionizing power so calculated leads one to the conclusion that the degree of dissociation of strong electrolytes is about the same as in water. This point of view is fully substantiated by the lowering of the freezing point of salts dissolved in pure hydrogen peroxide.

Certainly there is no evidence to show that the higher dielectric constant of the peroxide solutions markedly increases the ionizing power. In point of fact it is to be noted that in all three cases, *i. e.*, for dilutions 10, 50 and 100, if anything a minimum value for the ionizing power is obtained for the 35% solution whose dielectric constant is higher. Due however to the approximate character of the data definite statements cannot be made until more accurate values are obtainable. The only conclusion which appears justifiable, until more data are available, is that, due to the abnormally high values of the dielectric constant of water, hydrogen peroxide and its aqueous solutions, the ionizing power of these solvents is high and of a comparable magnitude.

The conductivity of the acetic acid in peroxide solutions is astonishingly small in the higher concentrations of peroxide and will be investigated more thoroughly before any comments are made.

Hydrogen peroxide shows a great similarity to water in many of its physical properties. Hence it will be of interest to make a thorough investigation of the conductivities of electrolytes in hydrogen peroxide as a medium.

Acknowledgment is made to the National Research Council of Canada for a bursary and studentship awarded to one of us, during the tenure of which the work was carried out.

Summary

The dielectric constants of hydrogen peroxide and its aqueous solutions were measured. It was shown that a maximum occurs at a concentration of 35% of H_2O_2.

The refractive indices of hydrogen peroxide solutions were measured over the whole range of concentration and at three wave lengths. The molecular refractive power and dispersive power indicate that the structure cannot be represented by two hydroxyl oxygens. It is suggested that the coordinate oxygen linkage which is given by Sugden's parachor has a definite atomic refractive power.

The polarizability as calculated from the refractive indices was shown to increase continuously with increased concentration of peroxide.

A method was described for measuring electric conductivities in hydrogen peroxide and its solutions.

Potassium chloride solutions were measured and the amount of dissociation was shown to be nearly the same as in water.

Acetic acid solutions were found to have far smaller conductivities than the corresponding solutions in water.

The specific conductivity of pure hydrogen peroxide was shown to be less than 2×10^{-6} and consequently it can be only very slightly dissociated.

MONTREAL, CANADA

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

THE PHOTOCHEMICAL FORMATION OF PHOSGENE

BY S. LENHER[1] AND G. K. ROLLEFSON

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A photochemical reaction which has been the subject of considerable interest during the last few years is the formation of phosgene from carbon monoxide and chlorine. The principal investigations on this reaction have been carried out by Bodenstein and his co-workers? They have shown that at room temperature the reaction rate is given by the expression

$$\frac{d(COCl_2)}{dt} = kI^{1/2}_{abs.}(Cl_2)\,(CO)^{1/2}$$

The quantum yield was found to be from 1000 to 3000 molecules of phosgene for every quantum of light absorbed by the chlorine. In the most recent paper cited above this is explained by a mechanism in which phosgene is formed by direct union of carbon monoxide and chlorine with chlorine atoms as a catalyst. It is the purpose of this paper to show that the observed rate law can be derived from a chain mechanism with fewer assumptions than were necessary in the previous case.

In the paper by Bodenstein, Lenher and Wagner the following set of reactions has been used in deriving the rate law

$$Cl_2 + h\nu = 2Cl \tag{1}$$
$$CO + Cl = COCl \tag{2}$$
$$COCl = Cl + CO \tag{3}$$
$$CO + Cl_2 + Cl = COCl_2 + Cl \tag{4}$$
$$COCl + Cl = CO + Cl_2 \tag{5}$$

Reaction 3 is obviously the reverse of (2) and it is assumed that the rates are such that the three substances, CO, Cl and COCl, can be considered to be present in their equilibrium concentrations. In order to account. for the inhibiting action of oxygen and the sensitized formation of carbon dioxide, the following reactions were used

$$COCl + O_2 = CO_2 + ClO \tag{6}$$
$$ClO + CO = CO_2 + Cl \tag{7}$$

The principal weakness in the above scheme is that it disregards the formation of phosgene by the action of chlorine on COCl. If the COCl reacts with oxygen as is indicated by (6), then it is certain to react with chlorine, which is a much more reactive substance than oxygen. The mechanism which we wish to present has the phosgene formed from COCl and chlorine at room temperature and retains the idea that the action of

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[1] National Research Fellow in Chemistry, 1928.

[2] (a) Bodenstein, *Z. physik. Chem.*, **130**, 422 (1927); (b) Schumacher, *ibid.*, 129, 241 (1927); (c) Bodenstein and Onoda, *ibid.*, 131, **153** (1927); (d) Bodenstein, Lenher and Wagner, *ibid.*, **3B**, 459 (1929).

the oxygen is on the COCl but does not consider that the COCl is present in its equilibrium concentration at room temperature.

For the first step in our mechanism we must consider that the chlorine molecule is dissociated by light.[3] The second step is the formation of COCl, which occurs by a triple collision as indicated by the equation

$$CO + Cl + M = COCl + M^1$$

where M is a molecule which takes up energy in the form of vibrational, rotational or kinetic energy sufficient in amount to stabilize the COCl molecule. The latter molecule reacts with chlorine to form a phosgene molecule and a chlorine atom. The rate of formation of phosgene in this way is considered to be so fast compared to the rate of decomposition of COCl that it may be considered the determining factor in fixing the concentration of COCl. For a chain terminating reaction we shall use Reaction 5 of the mechanism proposed by Bodenstein, Lenher and Wagner. The complete mechanism is therefore

$$Cl_2 + h\nu = 2Cl \qquad (I)$$
$$CO + Cl + M = COCl + M^1 \qquad (II)$$
$$COCl + Cl_2 = COCl_2 + Cl \qquad (III)$$
$$COCl + Cl = CO + Cl_2 \qquad (IV)$$

From an inspection of the proposed scheme it is not obvious what rate law can be derived, hence we shall make a rather detailed calculation of the rate law. The assumption back of this derivation is that the intermediate compounds, COCl and Cl, are present in steady state concentrations which are controlling factors in determining the rate. In the usual way we can calculate the steady state concentrations as follows

$$\frac{d(Cl)}{dt} = k_1 I_{abs.} + k_3(COCl)(Cl_2)$$

$$\frac{d(Cl)}{dt} - k_2(CO)(Cl)(M) + k_4(COCl)(Cl)$$

$$\frac{d(COCl)}{dt} = k_2(CO)(Cl)(M)$$

$$-\frac{d(COCl)}{dt} = k_3(COCl)(Cl_2) + k_4(COCl)(Cl)$$

$$(COCl) = \frac{k_2(CO)(Cl)(M)}{k_3(Cl_2) + k_4(Cl)}$$

In this case and in all others following where a term due to Reaction IV occurs in a sum with a term due to Reaction III, the principal chain reaction, we shall neglect the former. This is justified by the quantum yield, which shows that Reaction III occurs about one thousand times more frequently than Reaction IV. With this simplification, we obtain for the concentration of COCl

$$(COCl) = \frac{k_2(CO)(Cl)(M)}{k_3(Cl_2)}$$

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[3] The dissociation of molecules by light has been discussed by Franck, *Trans. Faraday Soc.*, 21, **536** (1925), and Franck, Kuhn and Rollefson, *Z. Physik*, 43, 155 (1927).

The concentration of chlorine atoms is obtained by equating d(Cl)/d*t* and $-$d(Cl)/d*t*, substituting for COCl where it occurs.

$$k_1I_{abs} + k_2(CO)\,(Cl)\,(M) = k_2(CO)\,(Cl)\,(M) + k_4\,\frac{k_2(CO)\,(Cl)^2\,(M)}{k_3(Cl_2)}$$

$$k_1I_{abs.} = k_4\,\frac{k_2(CO)\,(Cl)^2\,(M)}{k_3(Cl_2)}$$

$$(Cl)^2 = \frac{k_1k_3I_{abs.}(Cl_2)}{k_2k_4(CO)\,(M)}$$

$$(Cl) = \sqrt{\frac{k_1k_3I_{abs.}(Cl_2)}{k_2k_4(CO)\,(M)}}$$

Substituting the expression for (Cl) in the expression for COCl, we obtain

$$(COCl) = \frac{k_2}{k_3}\sqrt{\frac{k_1k_3I_{abs.}(CO)\,(MI}{k_2k_4(Cl_2)}}$$

The rate of formation of phosgene is

$$\frac{d(COCl_2)}{dt} = k_3(COCl)\,(Cl_2) = k_2\sqrt{\frac{k_1k_3I_{abs}\,(CO)\,(M)\,(Cl_2)}{k_2k_4}}$$

$$\frac{d(COCl_2)}{dt} = k^1I^{1/2}{}_{abs}\,(Cl_2)^{1/2}\,(CO)^{1/2}\,(M)^{1/2}$$

where $k^1 = k_2\sqrt{k_1k_3/k_2k_4}$. Comparing this equation with the experimental one given by Bodenstein,[2] we see that if we set (M) = (Cl_2) the two expressions are identical. Since M comes into the scheme in II as the substance which takes up the energy which the COCl must lose to become stable, the only condition which must be fulfilled for M to equal (Cl_2) is that chlorine should have a greater efficiency for such a process than carbon monoxide or phosgene. Such differences in efficiency in taking up energy are well known in the study of the extinction of fluorescence.[4]

Now that we write Equation II in our scheme as[5]

$$CO + Cl + Cl_2 = COCl + Cl_2^1$$

two questions arise, (a) why cannot Cl + Cl_2 in this reaction be written as Cl_3, and (b) why do we have COCl formed instead of phosgene as is the case in the mechanism proposed by Bodenstein, Lenher and Wagner? In regard to the first question, we can say that the experimental data available does not enable one to settle this question. If the Cl_3 can be considered to be present in its equilibrium concentration, then the two mechanisms are kinetically identical. Such an assumption must be considered improbable since the formation of the Cl_3 molecule must be through a triple collision and, therefore, the rate of formation probably is not very fast compared to the second order reactions which make up the following stages, hence the Cl_3 concentration would be below the equilibrium value. In such a case, the rate law would have to contain a factor corresponding to the

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[4] Geiger and Scheel, "Handbuch der Physik," Quanten XXIII, Julius Springer, Berlin, 1926.

[5] Cl_2^1 is an energy-rich chlorine molecule which dissipates its excess energy thermally.

third body involved in the triple collision. No evidence for such a factor has been obtained. Another possibility is that Cl_3 is formed as a quasimolecule[6] which reacts with the carbon monoxide, thus greatly increasing the number of collisions in which COCl is formed over the number which would be calculated on a simple kinetic theory basis. Such a mechanism would account for an extremely specific action on the part of chlorine. We feel, however, that the latter case is adequately covered by writing the equation as a triple collision which involves chlorine specifically rather than to write equations involving such indefinite substances as quasimolecules. At present, experiments are being carried out in the hope that the chlorine molecule may be replaced by some other molecule in this step.

Turning to the second question, we must consider the relative probabilities for the formation of COCl and phosgene in the triple collision. The formation of phosgene requires that the energy which must be removed from the phosgene molecule to stabilize the molecule must be converted into kinetic energy. The probability for the loss of energy of activation as kinetic energy is given by Frenkel and Semenoff as 10^{-4}.[7,8] If this figure is taken as applicable to energies of the magnitude we are concerned with, it means that the formation of phosgene would occur only once in ten thousand triple collisions of the kind we have. On the other hand, if we have COCl formed, the energy goes into both kinetic energy and energy of vibration and rotation of the chlorine molecule. Examining the data on the quenching of fluorescence by various gases we find that the diatomic gases are generally much more efficient than the monatomic gases.[9] A general quantitative comparison cannot be made because of various specific effects which are always present, but we can say that in a triple collision such as the one under consideration the most probable reaction is the one requiring a minimum amount of energy to be dissipated as kinetic energy, and in this case that is the formation of COCl. By this we do not mean to imply that no phosgene can be formed directly by such a triple collision but merely that at room temperature the amount of phosgene so formed is not sufficient to affect the rate law.

Bodenstcin, Lenher and Wagner avoid any consideration of the mode of formation of COCl by assuming that it is present at its equilibrium concentration. In view of the fact that the formation process must be considered a triple collision, we can apply the same argument against COCl existing in its equilibrium concentration that we have already applied to the assumption of Cl_3.

[6] Born and Franck, Z. *Physik,* **31,** 411 (1925).

[7] Frenkel and Semenoff, *ibid.,* 48, 216 (1928).

[8] Semenoff, *Z. physik. Chem.,* **2B,** 161 (1929).

[9] Pringsheim, "Fluorescenz und Phosphorescenz," Springer, Berlin, **1928,** 3d ed., p. 126.

For the chain terminating reaction we have retained the one used by Bodenstein, Lenher and Wagner, *i.* e.

$$COCl + Cl = CO + Cl_2$$

Since this is a bimolecular reaction, it must be considered as more probable than any reaction involving a triple collision or diffusion to the walls of the reaction vessel. We also wish to carry over Reactions 6 and 7 for the action of oxygen on the system, so our complete scheme for the photochemical reaction at room temperature becomes as follows

$$Cl_2 + h\nu = 2Cl \qquad \text{(I)}$$
$$CO + Cl + Cl_2 = COCl + Cl_2{}^{1} \qquad \text{(II)}$$
$$COCl + Cl_2 = COCl_2 + Cl \qquad \text{(III)}$$
$$COCl + Cl = CO + Cl_2 \qquad \text{(IV)}$$
$$COCl + O_2 = CO_2 + ClO \qquad \text{(V)}$$
$$ClO + CO = CO_2 + Cl \qquad \text{(VI)}$$

Let us now summarize the advantages of this scheme over the one previously presented. We have eliminated the necessity for the following assumptions: (a) that COCl reacts with oxygen but not with chlorine; (b) that COCl or any other substance is present in its equilibrium concentration; (c) that the formation of phosgene depends on a triple collision of a type known to have a low probability. In order to accomplish this, the sole assumption needed is that chlorine molecules shall have a relatively high efficiency in causing the formation of COCl. We feel, therefore, that our scheme is preferable since it rests on fewer assumptions.

At temperatures around 300° or higher it has been found[2b] that the rate law becomes

$$\frac{d(COCl_2)}{dt} = kI_{\text{abs.}}(Cl_2)\ (CO)$$

In order to account for this change it is considered that at high temperatures the rate of decomposition of COCl into carbon monoxide and atomic chlorine increases until it becomes fast compared with the other reactions involving COCl and, therefore, we can assume that under such conditions the COCl is present in its equilibrium concentration. We shall also assume that this equilibrium concentration is very small, thus accounting for the absence of CO_2 formation at the higher temperature, since reducing the COCl concentration to a low value reduces the rates of V and VI to very low values. Such a reduction in the COCl concentration must necessarily also reduce the rates of III and IV and, therefore, we must seek some reaction other than III as the source of phosgene. The only one permitted by our mechanism is that phosgene is formed by the triple collision of chlorine atom, chlorine molecule and carbon monoxide. At room temperature this source of phosgene has been considered subordinate to the formation by way of COCl. With the latter reaction eliminated this triple collision becomes the sole source of phosgene. Now in order for the rate of formation of phosgene at the higher temperature to be of the same order of magnitude as the room temperature rate, it is necessary for the concentration of chlorine atoms to increase. That this must occur is seen from the elimination of IV, which is the principal cause of the destruction of chlorine atoms in the room temperature reaction. With IV eliminated, the rate of disappearance of chlorine atoms will be determined by such factors as the rate of recombination at the wall or by collisions in the gas phase. These processes are subordinate to IV in the room temperature reaction but at the higher concentrations of chlorine atoms such as we have with IV out, the rates may become quite large. The work of Bodenstein, Lenher and Wagner at low pressures indicates that recombination at the wall is not much slower than IV, even under the conditions prevailing at room temperature. It is possible, however, that these rates are slow enough so that the concentration of chlorine atoms at high temperature is ten or a hundred times as great as it is in the presence of COCl. Such being the case, the amount of phosgene formed by the triple collision would be ten to a hundred times as great as before. For example, suppose that at room temperature one out of a hundred of the triple collisions yields phosgene, the other ninety-nine giving COCl; on raising the temperature this ratio between the amounts of COCl and phosgene formed remains the same but the COCl immediately decomposes without entering into any other reaction, leaving the phosgene, which appears at a measurable rate due to the increased number of collisions of the kind mentioned.

According to what has just been said, we attribute the high temperature formation of phosgene to the reaction

$$\mathrm{CO + Cl + Cl_2 = COCl_2 + Cl}$$

The rate of this reaction is given by

$$\frac{d(\mathrm{COCl_2})}{dt} = k_1(\mathrm{Cl})\ (\mathrm{Cl_2})\ (\mathrm{CO})$$

A comparison of this equation with the empirically determined rate equation shows that the two are identical if we can show that the concentration of the chlorine atoms is proportional to the amount of light absorbed. To prove such a proportionality rigorously requires more knowledge concerning factors controlling the rate of recombination of chlorine atoms than we possess. It is possible, however, to prove the relation for a special case. Suppose that the rate of disappearance of chlorine atoms is proportional to the number of collisions between the atoms and the wall. According to the kinetic theory this will be proportional to the partial pressure of the chlorine atoms. Thus we may write

$$\frac{-d(\mathrm{Cl})}{dt} = k_2(\mathrm{Cl})$$

For the formation of the atoms we may write

$$\frac{d(Cl)}{dt} = k_3 I_{abs.}$$

where k_3 is 2 if we give $I_{abs.}$ in quanta and consider that one quantum of light breaks a molecule into two atoms. Equating, we have

$$k_3 I_{abs.} = k_2(Cl)$$

or

$$(Cl) = \frac{k_3}{k_2} I_{abs.}$$

which is all we need to be able to write

$$\frac{d(COCl_2)}{dt} = kI_{abs.}(CO)\ (Cl_2)$$

where

$$k = \frac{k_1 k_3}{k_2}$$

It is quite possible that other methods of destroying the chlorine atoms will lead to the same result but, since we have no information concerning the details of such mechanisms, it is useless to attempt to make quantitative calculations.

Summary

A mechanism has been proposed for the photochemical formation of phosgene at room temperature involving COCl as an intermediate step. This mechanism has been compared with one proposed by Bodenstein, Lenher and Wagner involving COCl in a side reaction, and the assumptions involved in the two mechanisms have been discussed. **A** possible mechanism for the reaction above 300° has been suggested and discussed briefly.

BERKELEY, CALIFORNIA

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

SOLUTIONS OF SALTS IN PURE ACETIC ACID. II. SOLUBILITIES OF ACETATES[1]

BY ARTHUR W. DAVIDSON AND WALTER H. MCALLISTER

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Introduction

In the first paper of this series,[2] it was pointed out that anhydrous acetic acid is a far better solvent for salts than had been previously supposed, and existing data concerning solubilities and reactions of salts in this solvent were summarized. In the present investigation the solubilities of a number of typical acetates in acetic acid were measured over a wide range of temperature, and the compositions of all the compounds appearing as solid phases in these systems were determined. Although a number of addition compounds of acetates with acetic acid have been reported in the literature,[3] only two such systems, namely, those consisting of sodium and silver acetates in acetic acid, have been accurately investigated at more than one temperature.[4] In the present paper data are given for the acetates of potassium, ammonium, lithium, lead, barium and calcium. Other systems will be reported on in subsequent papers.

It has been shown by Kendall and co-workers[5] that, in polar solutions, compound formation between solute and solvent, or solvation, is a major factor in determining solubility, and further that in several series of systems of the type HX:RX, where the solute and solvent have a common anion, both solvation and solubility increase with increasing diversity in electropositive character between the metal R and hydrogen. It is to be expected, therefore, that in such a series solvation and solubility will be found to be greatest in the case of the salts of the alkali metals, less for those of the alkaline earth metals, while the salts of other metals, with few exceptions, are likely to be little solvated and not very soluble. The data here presented afford further opportunity for testing the validity of this view-point.

It has been repeatedly pointed out that any salt RX in solution in its own acid HX may be considered, formally at least, as a base.[6] That this

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[1] The material presented in this paper is from part of a thesis submitted by Walter H. McAllister to the Graduate School of the University of Kansas in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1929.

[2] Davidson, THIS JOURNAL, 50, 1890 (1928).

[3] References to these will be given later, in connection with the particular system under consideration. Hydrated compounds, however, will not be referred to.

[4] Kendall and Adler, THIS JOURNAL, 43, 1470 (1921).

[5] Kendall, Davidson and Adler, *ibid.*, 43, 1481 (1921). Cf. Hildebrand, "Solubility," Chemical Catalog Co., Inc., New York, 1924, pp. 118–120, 169–170.

[6] See, for instance, Schlesinger and Calvert, THIS JOURNAL, 33, 1924 (1911); also Ref. 5, p. 1494.

conception is of real significance, and not merely a matter of nomenclature, has recently been brought out very strikingly by the work of Hall and Werner,[7] who showed that sodium acetate could be titrated electrometrically with perchloric acid in acetic acid solution to a perfectly definite point of complete neutralization. According to Bronsted's conception of acids and bases,[8] the basicity of acetates is due to the strong tendency for the acetate ion to unite with a proton. Further evidence of the actual basicity of acetates in acetic acid will be presented in the latter part of this article.

Method

The freezing-point method was employed in this work for the determination of compound formation and solubility relationships. Solutions of known composition were prepared, cooled until crystallization occurred and then heated slowly, the temperature at which the last trace of crystals disappeared being recorded as the freezing point of the solution.[9] Freezing points below 100° were determined in large test-tubes provided with a thermometer and stirrer, suitable precautions being taken to exclude moisture. For solutions in which the equilibrium temperature was above 100°, small sealed bulbs were employed. Eight mercury thermometers were used, each of them having been calibrated either at fixed points or by comparison with certified thermometers. All temperatures were corrected for exposed stem. Each freezing point was determined at least twice.

Pure anhydrous acetic acid was prepared by the addition of the required amount of acetic anhydride to a special grade of C. P. glacial acetic acid, as described by Kendall and Gross.[10] The acid used in the determinations had a freezing point of 16.5 to 16.6°, which agrees with that given by Kendall and Gross for acetic acid of minimum conductivity.

Analysis of solvated compounds was unnecessary in those cases where the congruent melting point could be determined. In other cases, the compound was obtained in crystalline form by cooling a solution of appropriate composition, filtered off with the aid of suction and dried as rapidly as possible between porous tiles. The dried sample was then weighed and the acetic acid of solvation determined, except in the case of ammonium acetate, by titration with standard sodium hydroxide solution, using phenolphthalein as indicator. Neutral and solvated ammonium acetates were analyzed by adding concentrated sodium hydroxide solution to a weighed sample in a Kjeldahl flask, distilling the liberated ammonia into a measured amount of standard hydrochloric acid and titrating the excess acid with sodium hydroxide.

The results for the various systems are given below, and are represented also in the accompanying diagrams. Compositions are expressed in molecular percentages throughout; T denotes the equilibrium temperature.

Results

System Potassium Acetate–Acetic Acid.—Although no thorough study has been made of this system previously, two addition compounds

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[7] Hall and Werner, THIS JOURNAL, 50, 2367 (1928).

[8] Brönsted, *Chemical Reviews,* 5, 231 (1928), and previous papers.

[9] Details regarding method, apparatus and limits of accuracy have been given in earlier papers and need not be repeated here. See, for instance, Kendall and Landon, THIS JOURNAL, **42**, 2131 (1920).

[10] Kendall and Gross, *ibid*, **43**, 1426 (1921).

have been reported, $KC_2H_3O_2{\cdot}HC_2H_3O_2$,[11] melting at 148°, and $KC_2H_3O_2{\cdot}2HC_2H_3O_2$,[12] said to melt at 112°. The location of the eutectic point has also been studied.[13]

The salt used was prepared by neutralizing a solution of pure acetic acid with potassium hydroxide, crystallizing the salt from the solution and maintaining it at 180° for several days. The product had a melting point of 292°, agreeing with that previously reported.'' Since this salt is quite deliquescent, each sample was heated in the previously weighed freezing-point tube at 105° for several hours before weighing.

(a) Solid Phase $HC_2H_3O_2$

$KC_2H_3O_2$, %	0.0	1.22	2.11	6.70	7.62	9.10	10.03
T	16.50	15.82	15.30	10.95	9.71	7.45	5.95

(b) Solid Phase $KC_2H_3O_2{\cdot}2HC_2H_3O_2$

$KC_2H_3O_2$, %	10.97	11.36	1271	13.30	15.75	15.94	17.00
T	14.76	17.95	28.03	32.02	49.90	51.50	55.50
$KC_2H_3O_2$, %	17.92	18.71	19.00	20.48	23.72	23.85	
T	60.1	64 1	65.9	73.5	83.1	83.6	

(c) Solid Phase $KC_2H_3O_2{\cdot}HC_2H_3O_2$

$KC_2H_3O_2$, %	28.44	28.69	30.67	31.45	32.47	
T	99.0	101.2	110.0	114.0	118.0	
$KC_2H_3O_2$, %	33.44	33.94	34.41	34.65	35.00	35.27
T	121.0	121.5	124.5	125.5	126.0	126.0
$KC_2H_3O_2$, %	39.50	44.88	45.62	48.30	50.22	5232
T	137.0	145.0	146.0	147.5	148.0	147.5

(d) Solid Phase $KC_2H_3O_2$

$KC_2H_3O_2$, %	58.45	61.40	64.16	65.21	70.05	76.50	100.0
T	170	191	206	207	230	249	292

The curve for this system is given in Fig. 1. Analyses of the solid phase (b) gave a mean value for the acid content of 66.9 mole %, corresponding to the compound $KC_2H_3O_2{\cdot}2HC_2H_3O_2$.

The existence of the two acid salts previously reported has been confirmed. The melting point of 112° reported for the compound $KC_2H_3O_2{\cdot}2HC_2H_3O_2$ is erroneous, however, as this compound undergoes transition below its melting point, which, as indicated by extrapolation, would be about 100°. The compound $KC_2H_3O_2{\cdot}HC_2H_3O_2$ is stable up to its melting point, which is 148°, as reported by Melsens.

System Ammonium Acetate–Acetic Acid.—This system has not been studied previously, although isotherms for the ternary system ammonium

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[11] Melsens, *Compt. rend.*, **19**, 611 (1844).

[12] Lescoeur, *Ann. chim. phys.*, [6] *28*, 245 (1893).

[13] Vasiliev, *J. Russ. Phys.-Chem. Soc.*, *41*, 753 (1909).

[14] Schaffgotsch, ***Pogg. Ann.***, 102, 293 (1857).

acetate–acetic acid–water have been determined at 16 and 25°.[15] The compound $NH_4C_2H_3O_2 \cdot HC_2H_3O_2$, melting at 66.5°, has been reported.[16] Two different melting points have been reported for unsolvated $NH_4C_2H_3O_2$, 89° (which still is found in a number of standard reference books) and 112.5–114°.[16] The results of this work show the former to be entirely erroneous.

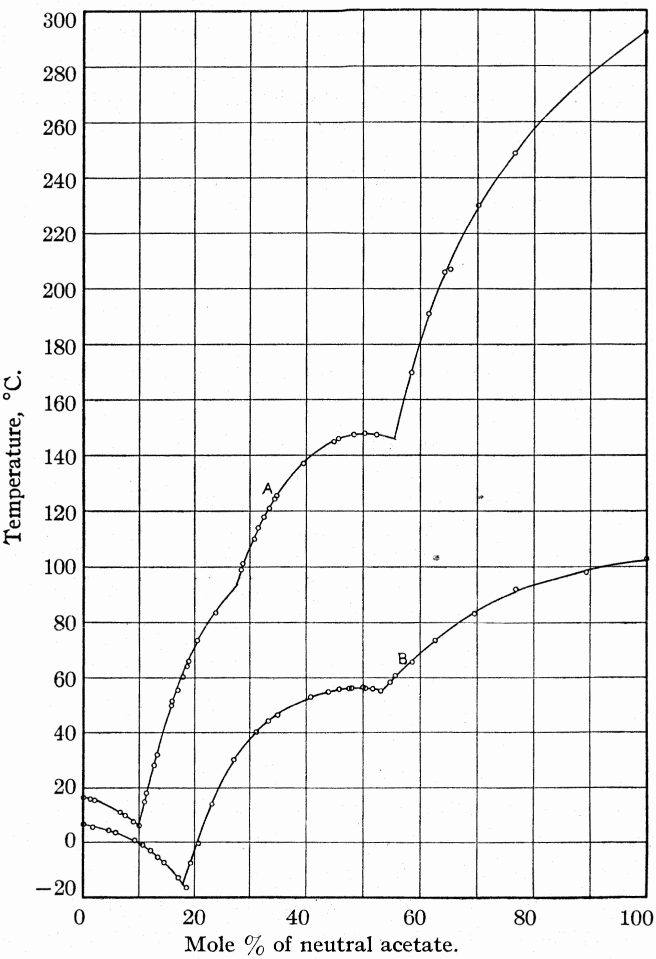

Fig. 1.—A, system $KC_2H_3O_2$–$HC_2H_3O_2$; B, system $NH_4C_2H_3O_2$–$HC_2H_3O_2$, add 10° to temperature scale.

No satisfactory method for the preparation of pure anhydrous ammonium acetate was found in the literature. The salt used was prepared

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[15] Sugden, J. *Chem. Soc.*, 960 (1926).

[16] Reik, *Monatsh.*, 23, 1033 (1902).

by passing dry ammonia gas (produced by the evaporation of liquid ammonia, to which metallic sodium had been added until the solution remained a deep blue color) over pure acetic acid contained in an evaporating dish over soda lime in a vacuum desiccator. After the mixture had solidified, it was pulverized and the process was continued for several days. The product obtained always analyzed within a few tenths of one per cent. of the theoretical 22.1% ammonia, and melted, in a sealed capillary tube, at 112–113°.

(a) Solid Phase $HC_2H_3O_2$

$NH_4C_2H_3O_2$, %	0.0	1.76	4.64	5.85	9.85	10.72
T	16.50	15.65	14.20	13.40	10.45	9.00
$NH_4C_2H_3O_2$, %	12 03	13.46	14.54	16 84	17.08	18.54
T	6.90	4.51	2.80	−2.5	−3.0	−6.5

(b) Solid Phase . $NH_4C_2H_3O_2 \cdot HC_2H_3O_2$

$NH_4C_2H_3O_2$, %	19.43	20.67	23.15	27 06	31 10	33 43
T	2.5	9.6	24.0	40.1	50 1	54 2
$NH_4C_2H_3O_2$, %	34.95	40.80	43.97	45.05	45 84	47 66
T	56.4	63.0	64.9	65.5	65.9	66 0
$NH_4C_2H_3O_2$, %	48.06	50.00	50.41	51.75	53.20	
T	66.2	66.5	66.2	66.0	65.2	

(c) Solid Phase $NH_4C_2H_3O_2$

$NH_4C_2H_3O_2$, %	54.83	55.60	58.70	62.63	69.50
T	68.5	70.8	75.7	83.6	93.0
$NH_4C_2H_3O_2$, %	76.84	89.25	100.0		
T	102	108	113		

The curve for this system is given in Fig. 1. The existence of the acid salt $NH_4C_2H_3O_2 \cdot HC_2H_3O_2$, which has been previously reported, is confirmed. This compound has a congruent melting point at 66.5°. The melting point of unsolvated $NH_4C_2H_3O_2$ is 113°.

System Lithium Acetate–Acetic Acid.—The compound $LiC_2H_3O_2 \cdot HC_2H_3O_2$, said to melt at 99°, has been reported.[17] The present work has shown this melting point to be erroneous. The location of the eutectic point in this system has been determined also.[13]

The salt used was prepared from a c. p. hydrate, which was recrystallized and then kept at 150° for three days. Its melting point, not previously reported, was found to be 272°.

(a) Solid Phase $HC_2H_3O_2$

$LiC_2H_3O_2$, %	0.0	3.56	3.81	5.01	5.72
T	16.50	14.85	14.80	14.16	13.75
$LiC_2H_3O_2$, %	6.86	7.57	7.70	8.45	
T	13.15	12 90	12.75	12.10	

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[17] Lescoeur, *Bull. soc. chim.*, **24**, 517 (1876); see also Ref. 12.

(b) Solid Phase $LiC_2H_3O_2 \cdot HC_2H_3O_2$

$LiC_2H_3O_2$, %	8.61	9.15	9.53	11.20	12.28	13.07
T	16.7	22.1	25.0	41.5	51.0	55.6
$LiC_2H_3O_2$, %	14.42	16.24	18.31	20 25	23.82	27.64
T	63.2	70.0	78.0	83.0	91.0	98.0
$LiC_2H_3O_2$, %	30.41	35.34	38.48	39.83	41.84	44.41
T	101.3	106.5	108.0	109.0	110.0[18]	111.0
$LiC_2H_3O_2$, %	45.32	45.74	46.77	48.76	50.06	
T	111.5	112.0	112.0	112.5	112.5	

(c) Solid Phase $LiC_2H_3O_2$

$LiC_2H_3O_2$, %	43.95	44.92	46.04	47.57	48.22	49.22
T	136.0	140.0	147.5	156.0	161.0	165.0
$LiC_2H_3O_2$, %	52.41	55.89	56.90	70.87	100.0	
T	178.5	188.0	192.0	221	272	

The curve for this system is given in Fig. 2. Analysis of the solid phase (b) gave a value for the acid content of 50.06 mole %, corresponding to the compound $LiC_2H_3O_2 \cdot HC_2H_3O_2$. The existence of the acid salt previously reported is thus confirmed. This compound undergoes transition before its melting point is reached, but its metastable melting point can readily be determined; it is 112.5°. The melting point of unsolvated lithium acetate is 272°.

System Lead Acetate–Acetic Acid.—This system has not been thoroughly studied previously, although a large part of the isotherm for the ternary system lead acetate–acetic acid–water at 25° has been determined.[19] Sandved states that it is impossible to bring about crystallization in very concentrated solutions of lead acetate in acetic acid. This was not found to be the case in the present work, although such solutions were exceedingly viscous and exhibited an enormous degree of supercooling, so that a great deal of patience was required in order to obtain satisfactory results with them.

The salt used was prepared from a c. p. hydrate by recrystallizing from dilute acetic acid and then drying over phosphorus pentoxide in a vacuum desiccator to constant weight, which required about six weeks. The product melted at 204°, agreeing with the figure previously reported.[20]

(a) Solid Phase $HC_2H_3O_2$

$Pb(C_2H_3O_2)_2$, %	0.0	0.54	5.18	8.42	11.53	19.78
T	16.50	16.33	15.52	14.24	13.40	9.55

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[18] Although the temperatures given here for systems containing from 40 to 50% $LiC_2H_3O_2$ correspond *to* a metastable equilibrium, these temperatures were invariably far easier to determine than those corresponding to the stable equilibrium between unsolvated $LiC_2H_3O_2$ and solution in this region. In fact, $LiC_2H_3O_2$ could be obtained from these solutions as solid phase only by seeding them with a crystal of this compound

[19] Sandved, *J. Chem. Soc.*, 2967 (1927).

[20] Petersen, *Z. Elektrochem.*, 20, 328 (1914).

$Pb(C_2H_3O_2)_2$, %	21.99	32.97	33.52	34.21	37.48	
T	8.05	−0.3	−0.8	−1.2	−3.1	
	(b) Solid Phase $Pb(C_2H_3O_2)_2$					
$Pb(C_2H_3O_2)_2$, %	35.69	38.27	38.46	41.43	41.75	44.95
T	49.0	68.0	0.2	87.3	88.0	100.5
$Pb(C_2H_3O_2)_2$, %	32.08	59.56	71.83	90.20	100.0	
T	119	139	165	192	204	.

The curve for this system is given in Fig. 2. Since it is a smooth curve from eutectic to melting point, no analysis was necessary. There are evidently no stable solvates. The melting point of $Pb(C_2H_3O_2)_2$ is 204°.

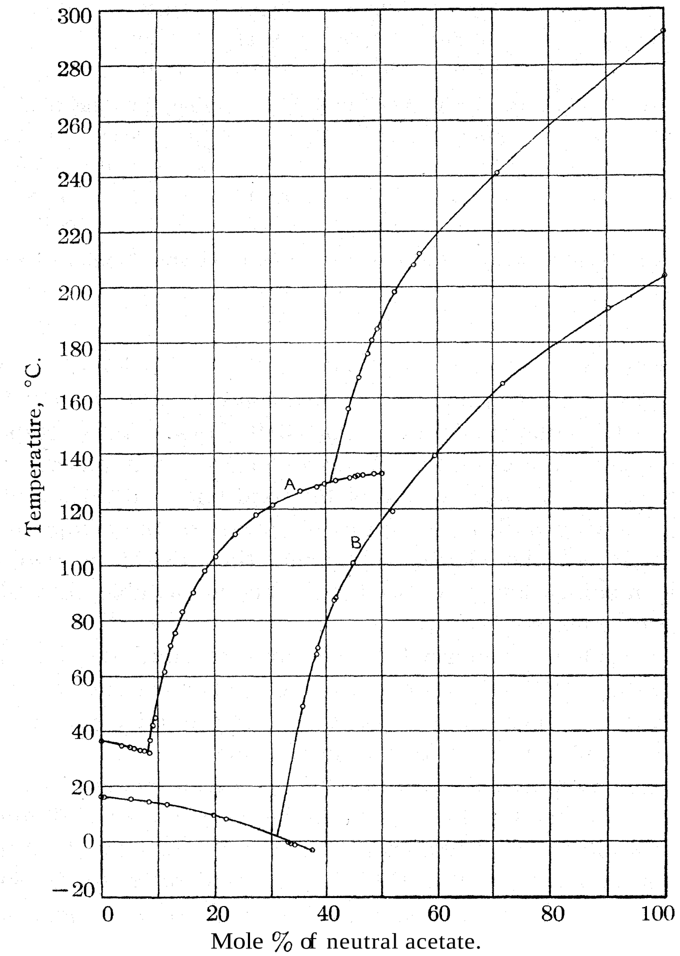

Fig. 2.—A, system $LiC_2H_3O_2$–$HC_2H_3O_2$, subtract 20° from temperature scale; B, system $Pb(C_2H_3O_2)_2$–$HC_2H_3O_2$

System Barium Acetate–Acetic Acid.—No previous work has been done on this system. A compound $Ba(C_2H_3O_2)_2 \cdot 2HC_2H_3O_2$ has been reported.[21]

The salt used was prepared by recrystallizing a C. P. hydrate from dilute acetic acid at 100° and keeping the product at 105° for several days.

(a) Solid Phase $HC_2H_3O_2$

$Ba(C_2H_3O_2)_2$, %	0.0	1.27	1.59	1.91	2.32	3.04
T	16.50	1.5.60	1543	1530	1500	14.63
$Ba(C_2H_3O_2)_2$, %	3.40	4.77	5.55	684	7.47	7.76
T	14.2	13.4	12.5	11.4	10.5	9.4

(b) Solid Phase $Ba(C_2H_3O_2)_2 \cdot 3HC_2H_3O_2$

$Ba(C_2H_3O_2)_2$, %	267	3.16	4.48	505	5.18	6.21
T	19.0	22.5	31.8	35.2	36.0	41.1
$Ba(C_2H_3O_2)_2$, %	6.86	7.53	8.11	8 62		
T	44.0	47.3	48.0	49 0		

(c) Solid Phase $Ba(C_2H_3O_2)_2 \cdot 2HC_2H_3O_2$ (Stable Modification)

$Ba(C_2H_3O_2)_2$, %	6.82	7.53	8.11	8.53	8.62	8.74	9.84
T	32.0	40.8	48.0	51.5	54.0	55.0	64.0
$Ba(C_2H_3O_2)_2$, %	11.37	11.70	12.46	14.06	15.08	15.58	
T	72.3	74.1	77.9	84.0	88.0	90.3	

(d) Solid Phase $Ba(C_2H_3O_2)_2 \cdot 2HC_2H_3O_2$ (Unstable Modification)

$Ba(C_2H_3O_2)_2$, %	8.11	9.70	10.78	11.37	11.88	12.38
T	13.8	19.9	24.3	27.1	29.8	32.0

The curve for this system is shown in Fig. 3. Analyses of the solid phase (b) gave a mean value for the acid content of 75.46 mole %, corresponding to the compound $Ba(C_2H_3O_2)_2 \cdot 3HC_2H_3O_2$. This compound has not been reported previously. Analyses of the solid phase (c) gave a mean value of 66.57 mole %, and of the solid phase (d), 65.69 mole % of $HC_2H_3O_2$, showing both these phases to consist of the compound $Ba(C_2H_3O_2)_2 \cdot 2HC_2H_3O_2$. The latter compound thus exists in two different crystalline modifications, one of them being metastable throughout the temperature range studied.

It was considered inadvisable to attempt to continue this curve beyond 16% $Ba(C_2H_3O_2)_2$ because of the high vapor pressure of acetic acid at the elevated temperatures required to bring about complete solution, in any reasonable time, at this concentration.

System Calcium Acetate–Acetic Acid.—Calcium acetate was reported to be little soluble in glacial acetic acid by Lescoeur.[22] Kendall and Adler[23] found its solubility to be less than 0.35 mole % of $Ca(C_2H_3O_2)_2$ at 30°. A compound $Ca(C_2H_3O_2)_2 \cdot HC_2H_3O_2$ has been reported by Colson.[24]

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[21] Iwaki, Mem. *Coll. Sci. Kyoto* Imp. *Univ.*, 1, 81 (1914); C. A., 10, 574 (1916).

[22] Ref. 12, p. 253.

[23] Ref. 4, p. 1478.

[24] Colson, *Compt.* rend., 137, 1061 (1903).

The salt used here was prepared in the same manner as the barium acetate.

(a) Solid Phase $Ca(C_2H_3O_2)_2 \cdot HC_2H_3O_2$

$Ca(C_2H_3O_2)_2$, %	0.0594	0 0670	0.0933	0.0968	
T	21.5	23.8	36.2	37.2	
$Ca(C_2H_3O_2)_2$, %	0.1576	0.2210	0.2823	0.3726	
T	52.5	60.9	67.6	75.1	
$Ca(C_2H_3O_2)_2$, %	0 4005	0.4935	0 5398	0 5573	
T	77.5	82.8	84.5	85 2	
$Ca(C_2H_3O_2)_2$, %	0 6287	0.6290	0.7082	0 9128	1.386
T	88.0	89.0	91.0	97.8	111.0

The curve for this system is shown in Fig. 3. Analyses of the solid phase (a) gave a mean value for the acid content of 50.66 mole %, corresponding to the compound $Ca(C_2H_3O_2)_2 \cdot HC_2H_3O_2$, which has been reported

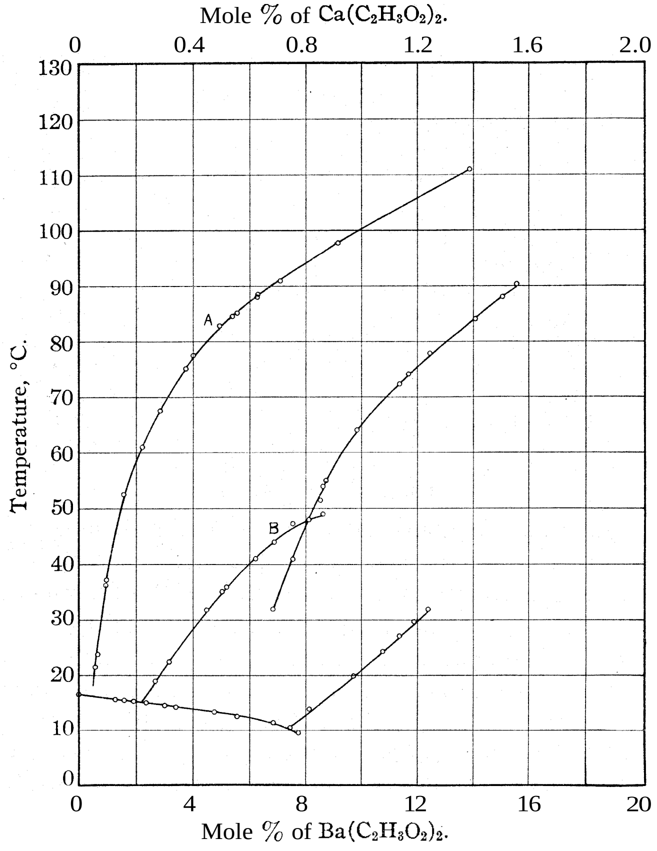

Fig. 3.—A, system $Ca(C_2H_3O_2)_2$–$HC_2H_3O_2$ (use upper concentration scale); B, system $Ba(C_2H_3O_2)_2$–$HC_2H_3O_2$ (use lower concentration scale).

previously. The curve was not continued beyond 1.4% of $Ca(C_2H_3O_2)_2$, for the same reason as in the case of the barium salt.

System Thallous Acetate–Acetic Acid.—The compound $TlC_2H_3O_2 \cdot HC_2H_3O_2$ has been reported.[25] Thallous acetate was prepared by the reaction between barium acetate and thallous sulfate in aqueous solution. After it had been dried for several days in a desiccator, the compound was found to melt at 127° (not 110°, as previously reported). The solubility was not accurately determined because of the limited quantity of salt available and its ready decomposition in sunlight. However, a rough determination showed the solubility to be approximately 2 mole % at 25°. The composition of the solid phase was not determined.

Summary of Data on Solvation and Solubility in Acetate–Acetic Acid **Systems.**—For ready comparison, the solvates which have been isolated in these systems, and the solubilities of acetates in pure acetic acid at 25°, are tabulated herewith.

Metal	Solvates isolated	Soly., mole per cent at 25°	Moles of $HC_2H_3O_2$ per mole of acetate in solid phase
K	$KC_2H_3O_2 \cdot 2HC_2H_3O_2$, $KC_2H_3O_2 \cdot HC_2H_3O_2$	12.29	2
NH_4	$NH_4C_2H_3O_2 \cdot HC_2H_3O_2$	23.46	1
Na[2]	$NaC_2H_3O_2 \cdot 2HC_2H_3O_2$, $NaC_2H_3O_2 \cdot HC_2H_3O_2$	7.06	2
Li	$LiC_2H_3O_2 \cdot HC_2H_3O_2$	9.37	1
Tl (-ous)	$TlC_2H_3O_2 \cdot HC_2H_3O_2$[25]	About 2	1
Ba	$Ba(C_2H_3O_2)_2 \cdot 3HC_2H_3O_2$ (not previously reported) $Ba(C_2H_3O_2)_2 \cdot 2HC_2H_3O_2$ (2 modifications)	3.48	3
Ca	$Ca(C_2H_3O_2)_2 \cdot HC_2H_3O_2$	0.068	1
Zn[26]	None	0.0018	0
Pb	None	31.9	0
Fe (-ic)[2]	None	Practically 0	0
Cu[26]	$Cu(C_2H_3O_2)_2 \cdot HC_2H_3O_2$	0.166	1
Ag[2]	None	0.094 (76°)	0

Discussion of Results

It is evident from the above table that solvation is most marked, and solubility is greatest, for the acetates of the most electropositive metals Only two of the acid salts isolated have been found to be sufficiently stable to reach their melting points before undergoing transition, namely, the 1:1 compounds of potassium and ammonium. The 1:2 compound of potassium, and the 1:1 compound of lithium (like the corresponding sodium compounds) undergo transition just before the melting point is reached. The high solubility of ammonium acetate is, of course, related to its low melting point. The solubility of lead acetate, even when its low melting point is taken into consideration, is surprisingly great.[27] This fact is

[25] Ref. 12, p. 249.

[26] From unpublished work in this Laboratory.

[27] Cf. Sandved, **Ref.** 19, p. 2974.

in line with the comparatively high solubility of the lead salts in other similar series, which was pointed out previously.[28]

Basic Properties of Acetates and of Water in Acetic Acid Solution.—Hall and Conant[29,30] studied the hydrogen-ion activity of glacial acetic acid solutions by means of the chloranil electrode and by their action upon indicators, and reached the tentative conclusion that the hydrogen-ion activity of pure glacial acetic acid can be represented by a P_H value in the neighborhood of zero[31] on a scale which is as yet an arbitrary one for this solvent, but which, it is hoped, may be found ultimately to coincide very nearly with the P_H scale in water. In the present investigation, qualitative experiments were made with a number of indicators which, according to Clark,[32] show color changes in water solution at a P_H value of about zero. We shall not take space here to report in detail the results of these experiments, especially since the names of the indicators are inadequate for complete identification, but shall merely summarize briefly the observations which we believe to be of interest. Acetic acid solutions of most of the indicators tried[33] showed definite color changes, in the direction of greater acidity (lower P_H), upon the addition of a small amount of a solution of dry hydrogen chloride in the same solvent. The original color of the indicator solution could then be restored, in every case, by the addition to the acid solution of a small amount of a solution of sodium or ammonium acetate. Other indicators[34] showed distinct color changes in the direction of greater basicity upon the addition of sodium or ammonium acetate, the original color being restored upon addition of hydrogen chloride solution. The acetates evidently act as bases in neutralizing acids in this solvent, the acetate ion of the base reacting with hydrogen ion of the acid to form undissociated acetic acid.

In this connection, it also seems worthy of mention that the behavior of water toward indicators was found to be similar to that of acetates, though less marked. Indicators in dilute solutions of dry hydrogen chloride or of anhydrous sulfuric acid in acetic acid could be restored to their "neutral" colors by the addition of a few drops of water. In other words, water, in acetic acid solution, behaves as a weak base. Such behavior is not surprising, since it has been pointed out repeatedly, in the work of Hantzsch and others, that water possesses basic properties be-

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[28] Kendall, Davidson and Adler, Ref. 5, p. 1501.

[29] Hall and Conant, THIS JOURNAL, 49, 3047 (1927).

[30] Conant and Hall, *ibid.*, 49, 3062 (1927).

[31] We wish to express our indebtedness to Dr. Hall for a private: communication touching upon this point.

[32] Clark, "The Determination of Hydrogen Ions," 3d ed., The Williams and Wilkins Co., Baltimore, 1928, pp. 76–86.

[33] Including crystal violet, methylene blue, alizarin blue, azorol green and safranine.

[34] Including methylene blue, benzopurpurin 4B and picric acid.

cause of its tendency to combine with hydrogen ion to form oxonium ion, OH_3^+.[35] In this respect water is quite analogous to ammonia, although the former is a somewhat weaker base because the OH_3^+ ion gives up its extra hydrogen ion, or proton, more readily than does the NH_4^+ ion. The behavior of ammonia and of water in acetic acid solution may be represented by the parallel equations

$$NH_3 + HC_2H_3O_2 \rightleftharpoons NH_4C_2H_3O_2 \rightleftharpoons NH_4^+ + C_2H_3O_2^-$$
$$H_2O + HC_2H_3O_2 \rightleftharpoons OH_3C_2H_3O_2 \rightleftharpoons OH_3^+ + C_2H_3O_2^-$$

In the latter case, the addition compound, which might be called oxonium acetate, must, indeed, be regarded as hypothetical, since it cannot be isolated in the solid state, even at low temperatures.[36] However, the existence of such a compound *in solution* appears quite probable from the fact that the cryoscopic effect of water in moderately dilute solution in acetic acid is practically identical with that of ammonia.[37] Thus, the curve obtained by plotting the freezing-point data of Rüdorff[38] for solutions of water in acetic acid, after recalculating the concentrations in terms of mole per cent. of $OH_3C_2H_3O_2$, coincides within the limit of experimental error, up to 5 mole per cent. of solute, with the curve found in the present investigation for $NH_4C_2H_3O_2$.[39] Although this method of comparison is admittedly imperfect,[40] and it is impossible to determine the degree of solvation of either ammonia or water in acetic acid solution from freezing-point depression data, nevertheless the exact coincidence of the two curves may be taken as a strong confirmation of the hypothesis that in this instance again, as in so many others, the parts played by water and by ammonia are essentially the same.

Summary

1. Freezing-point curves have been determined for binary systems consisting of acetic acid with the acetates of potassium, ammonium, lithium, lead, barium and calcium, and a number of addition compounds have been isolated and analyzed. Incidentally, a method has been given

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[35] For an outline of Hantzsch's results and other evidence for the existence of oxonium ion, see Hammett, THIS JOURNAL, 50, 2666 (1928). *Cf.* also Conant and Hall, Ref. 30, p. 3068.

[36] The complete freezing-point curve for the system H_2O–$HC_2H_3O_2$ is given by' Faucon, Ann. *chim. phys.*, [8] 19, 70 (1910). No compound appears as solid phase. *Cf.* Kremann, *Monatsh.*, 28, 893 (1907).

[37] The data of Hantzsch, *Z. physik. Chem.*, 61, 257 (1907), show the same thing to be true for solutions in sulfuric acid.

[38] Riidorff, ***Ber.*, 3,** 390 (1870).

[39] Obviously, the system $NH_4C_2H_3O_2$–$HC_2H_3O_2$ might have been regarded as a portion of the system NH_3–$HC_2H_3O_2$, in which case $NH_4C_2H_3O_2$ would have appeared as a 1:1 compound. The study of the latter system in its entirety is, however, beyond the scope of this work; it seemed preferable to choose $NH_4C_2H_3O_2$ and $HC_2H_3O_2$ as components in order to emphasize the analogy between ammonium and the alkali metals.

[40] *Cf.* Kendall, Booge arid Andrews, THIS JOURNAL, 39, 2308 (1917).

for the preparation of pure ammonium acetate, and the uncertainty as to the melting point of this salt has been cleared up.

2. Solvation and solubility in these systems, and in others of the same type for which data are available, have been found to be closely related, in accordance with the theories of Kendall.

3. Attention has been called to the basic properties of acetates in acetic acid solution, and to the similarity in function between ammonia and water in this solvent.

LAWRENCE, KANSAS

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

SOLUTIONS OF SALTS IN PURE ACETIC ACID. III. ZINC ACETATE AND SODIUM ZINC ACETATE[1]

BY ARTHUR W. DAVIDSON AND WALTER H. MCALLISTER

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Introduction

The solubility of zinc acetate in acetic acid was found by Kendall and Adler[2] to be very small, the saturated solution at 130° containing only about **0.1** mole per cent. of zinc acetate; no further data are given by these authors. In the first article of this series,[3] mention was made of the fact that the solubility of zinc acetate is greatly increased by the presence of sodium acetate, and it was pointed out that this was analogous to the behavior of zinc hydroxide, in aqueous solutions, upon the addition of sodium hydroxide; no quantitative work, however, has been done previously upon the ternary system sodium acetate–zinc acetate–acetic acid. In the present investigation the solubility of zinc acetate in acetic acid over a range of temperatures has been measured, both in the absence of sodium acetate and in the presence of increasing concentrations of the latter solute. Comparison of the results of these measurements with data given in the literature for the corresponding aqueous system has established the analogy between the two cases upon a firmer basis, and has made possible its further development, as will be shown below.

Method

Preparation of Materials.—The acetic acid employed was prepared as described in the preceding paper of this series. The sodium acetate was prepared by recrystallizing a C. P. hydrate from water and dehydrating it at 150° for about a week. Zinc acetate, it was found, could not be dehydrated even at temperatures as low as 90° without slow partial decomposition to a basic salt. The pure salt was made by re-

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[1] The material presented in this paper is from part of a thesis submitted by Walter H. McAllister to the Graduate School of the University of Kansas in partial fulfilment of the requirements for the degree of Doctor of Philosophy, **1929.**

[2] Kendall and Adler, THIS JOURNAL, 43, **1470** (1921).

[3] Davidson, **ibid.,** 50, 1890 (1928).

crystallizing the hydrate from dilute acetic acid, heating to 85–90° for several days, and then moistening the slightly basic product with pure acetic acid and heating again to 85° for six hours. A sample of this product showed, upon analysis carried out as described below, 35.64% of zinc (calcd. for $Zn(C_2H_3O_2)_2$, 35.65%).

Binary System.—The method used for determining the solubility of zinc acetate in pure acetic acid was the same as that described for other acetates in the preceding paper. Because of the very small solubility, in this case, and the very minute amount of solid which separated on cooling, the determination of the equilibrium temperature was somewhat troublesome. Nevertheless, with a reasonable amount of care, the temperatures were found to be reproducible, and those given are believed to be correct to within 0.5°.

Ternary System.—In the study of the ternary system, acetic acid solutions were prepared containing exactly 1, 2.5, 5 and 7 mole per cent., respectively, of sodium acetate. To these solutions increasing amounts of zinc acetate were added, and the equilibrium temperatures were determined just as in the binary systems. These temperatures were then plotted as ordinates against the mole percentages of zinc acetate as abscissas to give a series of curves, each individual one of which should represent the solubility of zinc acetate in a solution having a fixed value of the ratio, number of moles of sodium acetate/number of moles of (sodium acetate + acetic acid). To save space this mole ratio will subsequently be referred to simply as R.

Methods of Analysis.—Samples of the solid phases present at equilibrium were obtained by crystallization from the solutions under suitable conditions, followed by filtration and drying on porous tile as in previous work. In these cases, however, it was found to be impracticable to determine the acetic acid by direct titration, no accurate end-point being obtainable in the presence of zinc ion.[4] Analysis of these compounds was therefore carried out by the following means. In the case of the binary system the weighed sample was dissolved in water and the zinc determined by potentiometric titration at 65° with fortieth molar potassium ferrocyanide solution containing 0.1% potassium ferricyanide; this determination was sufficient to fix the composition of the compound. In the ternary system, however, it was necessary to determine a second constituent also. The acetates in the weighed sample were changed to sulfates by treatment with concentrated sulfuric acid, followed by heating to drive off acetic acid and excess sulfuric acid. The residue of sulfates was weighed, dissolved in water and zinc determined by potentiometric titration as above. The weight of zinc acetate in the original sample could be calculated directly from this titration, that of sodium acetate from the amount of sodium sulfate found by difference in the mixed sulfates, and acetic acid by difference between the total weight of the sample and the combined weights of zinc and sodium acetates.

The data obtained are tabulated below, and are represented also in the accompanying diagrams. The concentration of zinc acetate in the solution is expressed throughout in mole percentage; T is the equilibrium temperature.

A, BINARY SYSTEM $Zn(C_2H_3O_2)_2$–$HC_2H_3O_2$

(a) Solid phase $Zn(C_2H_3O_2)_2$

$Zn(C_2H_3O_2)_2$, %	0.0050	0.0054	0.0085	0.0109
T	40.5	43	48	52
$Zn(C_2H_3O_2)_2$, %	0.0150	0.0231	0.0382	
T	56	62	72	

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[4] An approximate determination could be made by potentiometric titration with sodium hydroxide solution, using a saturated quinhydrone electrode, but preliminary experiments showed the end-point obtained to be unreliable.

The curve for this system is given in Fig. 1. Due to the extremely small solubility of zinc acetate at low temperatures, it was found to be practically impossible to determine equilibrium temperatures below 40°. Enough points were obtained at higher temperatures, however, to make it possible to continue the curve to the eutectic point, with some degree of confidence, by extrapolation. The solubility at 25° appears to be 0.0018 mole per cent.

For the same reason, the solid phase (a) could not be obtained in sufficient quantity to afford as accurate an analysis as might be desired. However, analysis of a sample weighing 0.0720 g. showed **36.53%** of zinc (calcd. for $Zn(C_2H_3O_2)_2$, 35.65%). The compound, therefore, is evidently unsolvated $Zn(C_2H_3O_2)_2$.

B. TERNARY SYSTEM $NaC_2H_3O_2$–$Zn(C_2H_3O_2)_2$–$HC_2H_3O_2$

1. Mole Ratio R = 0.01. (a) Solid Phase $Zn(C_2H_3O_2)_2$

$Zn(C_2H_3O_2)_2$, %	0.323	0.376	0.417	0.463	0.487
T	35.5	65	73	78	82

2. Mole Ratio *R* = 0.025. (a) Solid Phase $Zn(C_2H_3O_2)_2 \cdot 2NaC_2H_3O_2 \cdot 4HC_2H_3O_2$

$Zn(C_2H_3O_2)_2$, %	0.445	0.495	0.588	0.646	0.764
T	26.1	26.3	26.1	27.0	28.0
$Zn(C_2H_3O_2)_2$, %	0.862		0.865		
T	27.8		28.0		

(b) Solid Phase $Zn(C_2H_3O_2)_2$

$Zn(C_2H_3O_2)_2$, %	0.895	0.919	1.028	1.123
T	30	36	72	82

3. Mole Ratio R = 0.05. (a) Solid Phase $Zn(C_2H_3O_2)_2 \cdot 2NaC_2H_3O_2 \cdot 4HC_2H_3O_2$

$Zn(C_2H_3O_2)_2$, %	0.251	0.442	0.487	0.594	0.625	0.666
T	25.0	29.2	29.1	31.7	32.5	33.5
$Zn(C_2H_3O_2)_2$, %	0.701	0.763	0.809	0.852	1.106	2.162
T	33.5	35.0	35.5	36.7	39.8	42.0

4. Mole Ratio *R* = 0.07. (a) Solid Phase $Zn(C_2H_3O_2)_2 \cdot 2NaC_2H_3O_2 \cdot 4HC_2H_3O_2$

$Zn(C_2H_3O_2)_2$, %	0.247	0.294	0.464	0.469	0.662
T	26.7	28.5	33.9	33.2	36.1
$Zn(C_2H_3O_2)_2$, %	0.903	1.030	1.318	1.927	
T	41.2	42.7	46.0	48.6	

The curves for this system are given in Fig. 1. It is immediately evident that these curves exhibit a marked change in slope with change in the solid phase in equilibrium with the solution. The solid phase 1 (a) could not be obtained in sufficient amount for analysis, but it seemed certain, from their similarity in appearance and behavior, that it was the same as solid phase 2 (b). Analyses of the latter gave a mean value of 35.45% of zinc, which showed that the compound was unsolvated $Zn(C_2H_3O_2)_2$. Again, it seemed probable from the similarity in their appearance and in the slope of the corresponding curves that solid phases 2 (a), **3** (a) and 4 (a) were identical. Analyses gave the following figures:

Solid **phase**	Mole % of $Zn(C_2H_3O_2)_2$	Mole % of $NaC_2H_3O_2$	Mole % of $HC_2H_3O_2$
2(a)	14.38	29.45	56.17
3(a)	14.37	29.84	55.79
4(a)	13.33	27.80	58.88
Calcd. for $Zn(C_2H_3O_2)_2\cdot$-$2NaC_2H_3O_2\cdot 4HC_2H_3O_2$	14.29	28.57	57.14

Considering the difficulties involved in freeing these solid phases completely from the mother liquor, their instability in moist air and the necessity of determining one of the constituents by difference, these figures, it is believed, establish satisfactorily that the substances are all identical

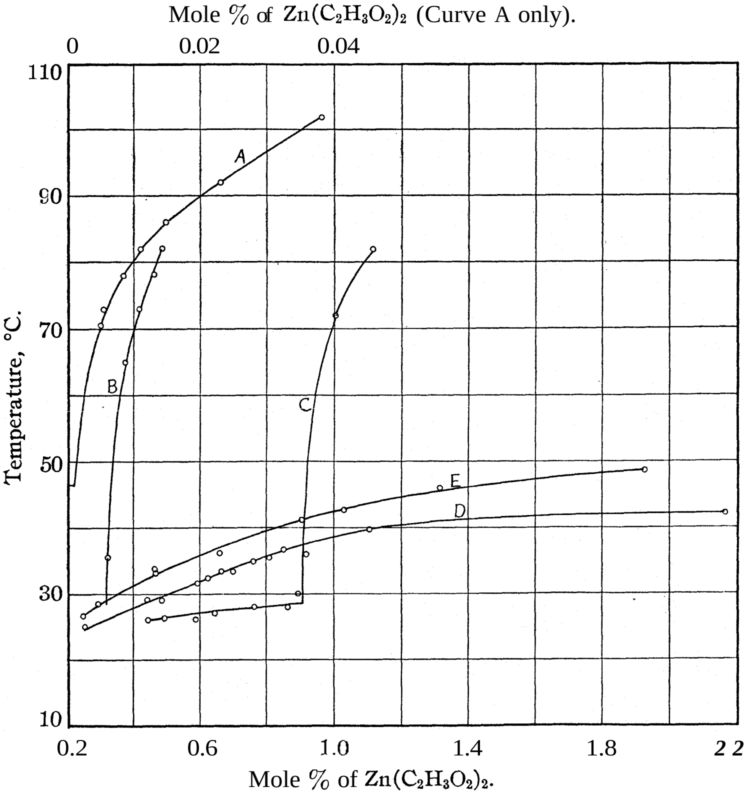

Fig. 1.—Solubility curves of $Zn(C_2H_3O_2)_2$ in pure $HC_2H_3O_2$ and in the presence of various concentrations of $NaC_2H_3O_2$. **A,** R = 0.00 (pure acetic acid); subtract 30° from temperature scale. B, R = 0.01; C, R = 0.025; D, R = 0.05; E, R = *0.07.*

and consist of a ternary compound, or solvated sodium zinc acetate, of the composition given.

It now becomes apparent that the solubility of zinc acetate in acetic acid at a fixed temperature increases with increasing concentration of sodium acetate, so long as zinc acetate itself is the stable solid phase. Upon the appearance of the ternary compound, however, the mole percentage of zinc acetate in the saturated solution begins to decrease with increase in concentration of sodium acetate. This is brought out more clearly in Fig. 2, which shows an isotherm for 28.5°, plotted from data obtained from the curves in Fig. 1. Here the solubility of zinc acetate, which is only 0.0022 mole per cent. in pure acetic acid, increases upon the addition of sodium acetate until R is 0.025, where the solubility reaches a maximum of 0.91 mole per cent. At this point the solution can exist in equilibrium with both solid phases. Then with further addition of sodium acetate the mole percentage of zinc acetate in the saturated solution falls off, becoming 0.30 for R = 0.07. At slightly higher values of R, the compound $NaC_2H_3O_2{\cdot}2HC_2H_3O_2$ appears as solid phase. The investigation was not continued into this region.

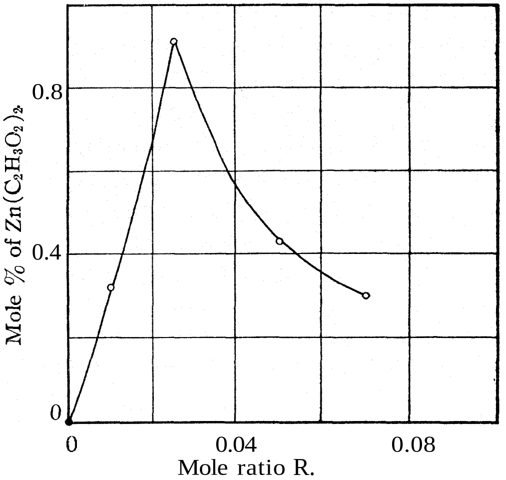

Fig. 2.—Effect of increasing concentrations of $NaC_2H_3O_2$ upon the solubility of $Zn(C_2H_3O_2)_2$ in $HC_2H_3O_2$ at a fixed temperature; isotherm at 28.5°.

Comparison of Results with Data for the Corresponding Aqueous System.—The system $Zn(OH)_2$–NaOH–H_2O has been studied quantitatively by a number of investigators.[5] Although the data of the various workers show rather poor agreement,[6] it has been observed in every case that the solubility of zinc hydroxide at a fixed temperature at first increases with increasing concentration of sodium hydroxide. Whenever the investigation has been continued up to very high concentrations of sodium hydroxide, however, a new solid phase, referred to in every case

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[5] The most recent and apparently the most reliable of these studies are the following: (a) Goudriaan, *Rec. trav. chim.*, **39, 505** (1920); (b) Muller, Z. *Elektrochem.*, **33, 135** (1927); (c) Dietrich and Johnston, THIS JOURNAL, **49,** 1419 (1927); **(d)** Fricke, *Z. anorg. allgem. Chem.*, *172, 234 (1928).*

[6] Due, according to Dietrich and Johnston (Ref. 5c, p. 1423), to the fact that in most cases the exact nature of the solid phase is open to question.

as sodium zincate, has been found to appear,[7] and from this point on the concentration of zinc hydroxide in the saturated solution decreases with further addition of sodium hydroxide. Obviously, from the data obtained in the present investigation, the relationships in the corresponding ternary system in acetic acid are quite analogous to those just discussed, with the ternary addition compound which occurs in the acetic acid system playing the same part as the sodium zincate in the aqueous system.[8]

This analogy now naturally brings up the question of the composition of the solid phase referred to as sodium zincate. Here again there is no agreement between the results of different investigators. Selecting those which appear to be the most reliable, we find the following formulas reported for compounds of this type: (1) $NaHZnO_2 \cdot 3H_2O$,[9] (2) $Na_2ZnO_2 \cdot 4H_2O$,[10] (3) $NaHZnO_2 \cdot 4H_2O$.[11] Still other compounds of this nature have been reported by other investigators.[12] All of these so-called sodium zincates, however, have this property in common, namely, that they may be formulated as addition compounds, generally hydrated, of the two hydroxides. Thus the formulas of the three listed above may be rewritten as follows: (1) $Zn(OH)_2 \cdot NaOH \cdot 2H_2O$, (2) $Zn(OH)_2 \cdot 2NaOH \cdot 2H_2O$, (3) $Zn(OH)_2 \cdot NaOH \cdot 3H_2O$. The similarity between such formulas and that of the solvated sodium zinc acetate isolated from the acetic acid system in this investigation is plainly evident. The resemblance between the latter compound and the hydrated disodium zincate of Goudriaan[10] is particularly close, as appears in the following comparison:

$$Zn(OH)_2 \cdot 2NaOH \cdot 2H_2O \text{ or } Na_2ZnO_2 \cdot 4H_2O$$
$$Zn(C_2H_3O_2)_2 \cdot 2NaC_2H_3O_2 \cdot 4HC_2H_3O_2 \text{ or } Na_2Zn(C_2H_3O_2)_4 \cdot 4HC_2H_3O_2$$

Discussion

It has been customary to attribute the reaction between zinc hydroxide and sodium hydroxide in aqueous solution to the so-called amphoteric nature of zinc hydroxide. This compound is thought of as possessing weakly acidic as well as weakly basic properties and as being capable, by virtue of the former, of reacting with bases to form zincates. The same point of view and system of nomenclature have been carried over

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[7] At 30°, according to Müller (Ref. 5 b, p. 140), this occurs when the concentration of sodium hydroxide reaches about 12 moles per liter. Dietrich and Johnston found only zinc hydroxide as solid phase, their investigation not having extended to concentrations of alkali sufficiently high for the appearance of sodium zincate.

[8] It should be noted that, just as the sodium zincate is unstable in the presence of water, changing to zinc hydroxide, so the ternary compound is unstable in pure acetic acid, changing to zinc acetate.

[9] Foerster and Günther, *Z. Elektrochem.*, 6, 301 (1899).

[10] Goudriaan, Ref. 5a, p. 508.

[11] Fricke, Ref. 5d, p. 242.

[12] See Comey and Jackson, *Am. Chem. J.*, 11, 145 (1899); also Muller, Ref. 5b, p. 139.

to the ammonia system of compounds.[13] Thus, when it was found by Fitzgerald that zinc amide reacted with a liquid ammonia solution of potassium amide to give a crystalline product whose formula could be written $Zn(NH_2)_2 \cdot 2KNH_2$, or $Zn(NHK)_2 \cdot 2NH_3$,[14] this new compound was immediately named potassium ammonozincate, and its formation was cited as evidence of the amphoteric nature of zinc amide.[15] With these precedents in mind, and in view of the composition and mode of formation of the new compound, $Zn(C_2H_3O_2)_2 \cdot 2NaC_2H_3O_2 \cdot 4HC_2H_3O_2$, obtained in the present investigation, it would appear to be entirely logical to call this compound, provisionally at least, sodium acetozincate, and to regard its existence as supplying further confirmation of the amphoteric nature of zinc. It must be borne in mind, however, that no evidence has as yet been obtained for the presence, in acetic acid solution, of analogs of the zincate ions, ZnO_2^{--} and $HZnO_2^{-}$, which are supposed to exist in aqueous solution. Preliminary experiments have indicated that the solubility of a number of other acetates in acetic acid is also increased by the presence of sodium acetate. Further investigation of these systems will be necessary, therefore, before it can be decided whether or not the concept of amphoterism[15b] affords the most satisfactory interpretation of their behavior.

Reactions of Zinc Salts in Acetic Acid Solution.—The quantitative study of solubilities reported above was supplemented by a few further experiments of a qualitative nature, the results of which appear to the writers to be of sufficient interest to warrant brief description here.

Metallic zinc did not react noticeably with pure acetic acid at room temperature; on heating, a slight reaction occurred, with the evolution of hydrogen and the appearance of insoluble zinc acetate. With a solution of dry hydrogen chloride, zinc reacted fairly readily, giving a clear solution; after a time a precipitate appeared, doubtless consisting of zinc chloride. With a solution of sodium acetate zinc gave no noticeable reaction until the mixture was heated, when the evolution of hydrogen took place more rapidly than with pure acetic acid; in this case no insoluble product was formed. This last reaction appears to be analogous to the action upon zinc of aqueous sodium hydroxide solution.

Zinc acetate dissolved readily in the calculated amount of hydrogen chloride solution to give a clear solution of zinc chloride, which was used in the following tests. When a small amount of ammonium acetate solu-

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[13] See Franklin, Am. *Chem.* J., 47, 307 (1912), and THIS JOURNAL, 37, 2295 (1915).

[14] Fitzgerald, *ibid.*, 29, 656 (1907); see also Franklin, *ibid.*, 29, 1274 (1907). It should be mentioned that this compound is stable in the presence of liquid ammonia, in which it is but slightly soluble.

[15] (a) Franklin, *ibid.*, 35, 1455 (1913). See also (b) Kraus, Trans. Am. *Electrochem. Soc.*, *45*, 175 (1924), where the concepts of amphoterism and amphoteric properties of elements are discussed at some length.

tion was added to zinc chloride, a heavy precipitate of zinc acetate was formed after a few minutes. This precipitate dissolved readily in excess ammonium acetate. Similarly, a small amount of sodium acetate solution, added to zinc chloride, produced a precipitate[16] which dissolved readily in excess sodium acetate. Thus, just as zinc hydroxide, insoluble in water, dissolves in hydrochloric acid or in aqueous sodium or ammonium hydroxide, so zinc acetate, insoluble in acetic acid, dissolves in a solution of hydrogen chloride or of sodium or ammonium acetate in this solvent.

The precipitation of zinc sulfate upon the addition of sulfuric acid solution to zinc chloride, and of zinc sulfide upon the introduction of gaseous hydrogen sulfide, have been mentioned previously.[17] The latter precipitate was found to occur even in the presence of a small concentration of hydrogen chloride, but took place more readily in the absence of the latter, that is, in what might be spoken of as a "neutral" solution.[18] The precipitate dissolved when excess of hydrogen chloride solution was added.

Solutions of sodium oxalate and of orthophosphoric acid gave with zinc chloride white precipitates of the oxalate and phosphate, respectively, both of which dissolved readily in hydrogen chloride solution.

It may be noted that all of these qualitative observations, as well as those reported previously, point toward the generalization that if a salt is insoluble in water, it will be found to be insoluble in acetic acid also; if it is readily soluble in water, however, it may or may not be soluble in acetic acid.

Summary

1. The solubility of zinc acetate in pure acetic acid and in the presence of concentrations of sodium acetate up to about 7 mole per cent. has been determined at various temperatures.

2. The concentration of zinc acetate in the saturated solutions has been found to increase with increasing concentration of sodium acetate as long as zinc acetate itself is the stable solid phase, but to decrease with further addition of sodium acetate after the appearance of an addition compound as solid phase.

3. A solvated sodium zinc acetate of the formula $Zn(C_2H_3O_2)_2 \cdot 2NaC_2H_3O_2 \cdot 4HC_2H_3O_2$ has been isolated and analyzed.

4. Attention has been called to the marked analogy between the ternary system here studied and the corresponding aqueous system.

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[16] In this case the precipitate was obtained more readily from a zinc chloride solution prepared by heating hydrogen chloride solution with excess zinc acetate and filtering.

[17] Ref. 3, p. 1893.

[18] In this connection, it is worthy of note that cobalt and nickel sulfides could be precipitated from dilute solutions of their chlorides only in "basic" solution, that is, in the presence of sodium acetate, for example.

5. Some further reactions of zinc salts in acetic acid solution have been described.

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

PHOTOCHEMICAL STUDIES. X. THE ELECTRONIC AND PHOTOCHEMICAL DECOMPOSITIONS OF POTASSIUM CHLORATE

BY JOHN G. MEILER AND W. ALBERT NOYES, JR.

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The chemical effects of alpha and beta particles have been studied in some detail during the past few years.[1] These studies have served to demonstrate an equivalence between the extent of ionization and the amount of chemical reaction produced. It has also been shown[2] that reactions initiated by electron bombardment obey laws very similar to those applicable to a-particles. Other reactions have been studied in an effort to determine the minimum kinetic energy of electron which will produce an effect. Thus ammonia is formed in a mixture of nitrogen and hydrogen when these gases are under the influence of electrons of speed greater than those corresponding to the ionization potentials of both reacting gases.[3]

The present work was undertaken with the object of ascertaining whether solid potassium chlorate could be decomposed by slow speed electrons and to ascertain whether any relationship could be found between the kinetic energy of the electrons and the wave length of radiation necessary to bring about photochemical decomposition. The conditions for photochemical decomposition have been obtained, but the results on the electronic decomposition are somewhat less conclusive. They indicate, however, that solid potassium chlorate may be decomposed by fairly high speed electrons.

I. Experimental Procedure'

(a) The Electronic Decomposition.—Preliminary studies[4] indicated that solid oxalic acid could be decomposed by electron bombardment

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[1] For review, see Lind, "The Chemical Effects of Alpha Particles and Electrons," 2d ed., The Chemical Catalog Co., Inc., New York, 1928.

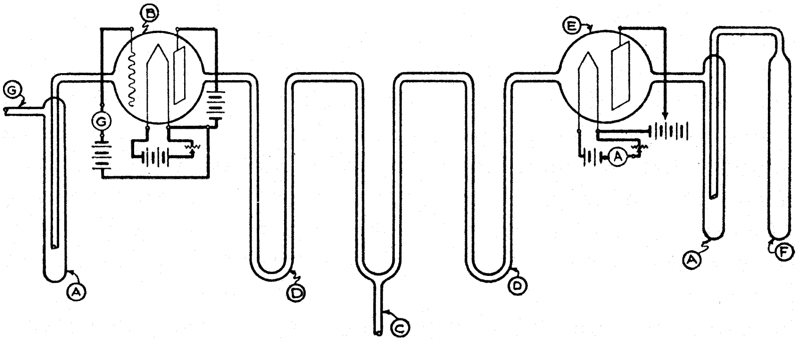
[2] See, for example, Marshall, THIS JOURNAL, 50, 3178 (1928); Busse and Daniels *ibid.*, 50, 3271 (1928); Kruger and Moeller, *Physik. Z.*, 13, 1040 (1912); Kruger and Utesch, *Ann. Physik*, 78, 113 (1925).

[3] Hiedeman, *Chem.-Ztg.*, 45, 1073 (1921); 46, 97 (1922); Anderson, *Z. Physik*, 10, 54 (1922); Storch and Olson, THIS JOURNAL, 45, 1605 (1923).

[4] For mention, see Noyes and Vaughan, *Chem. Reviews*, (to appear in the near future)

when the kinetic energy of the electrons exceeded a value corresponding to between 4.5 and 5.5 volts. In this study a filament was used as a source of electrons and their speeds were limited by grids in the ordinary way. The results obtained were open to question for the following reasons: (1) the charge on the solid may have rendered the velocity of the electrons uncertain; (2) oxalic acid does not have a negligible vapor pressure at room temperature;[5] (3) thermal radiation from the filament may have caused a slight amount of decomposition. This error was probably small.

To meet these objections partially it was decided to undertake a similar study of solid potassium chlorate, since it has a negligible vapor pressure at ordinary temperatures. Moreover, it undergoes a decidedly exothermic decomposition, which should cause any decomposition initiated by an electron to be magnified by an expected chain reaction.



A, Liquid-air trap; B, ionization gage; C, mercury shut-off; D, liquid-air trap; E, reaction vessei immersed in liquid air; F, mercury reservoir; G, to McLeod gage and pumps.

Fig. 1.—Schematic diagram of apparatus.

The method used in the electronic decomposition of solid potassium chlorate is similar to that used in work on critical potentials. It was necessary to simplify the apparatus by omitting the grids in order to increase the electron current.

Figure 1 shows a schematic diagram of the apparatus used. It was attached to the usual high vacuum line. The vacuum attainable was limited only by the vapor pressure of mercury at liquid-air temperatures (below 10^{-9} cm.).[6] The ionization gage (B) was the Poindexter modifications of the Buckley type,[7] depending on the ionization of the gas by electrons. The volume was only 250 cc., due to the necessity of developing an apparatus which could be thoroughly outgassed by baking in a furnace. The ionization gage was capable of measuring changes in pressure of 10^{-8} cm.

The reaction vessel was a two-electrode vacuum tube (E). The source of electrons was a hot filament in the shape of a spiral one centimeter in length containing three

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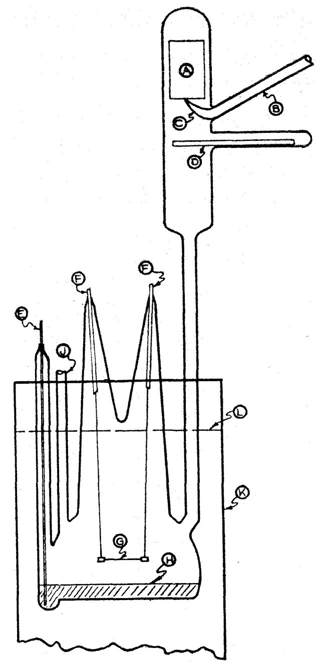
[5] Noyes and Wobbe, THIS JOURNAL, 48, 1882 **(1926).**

[6] Poindexter, **Phys. Rev., 26, 849 (1925).**

[7] Buckley, *Proc. Nat.* **Acad.** *Sci.*, **2, 683** (1916)

centimeters of tungsten wire. The first tubes had a metallic plate. It was found, however, that the potassium chlorate decomposed slightly before it was subjected to bombardment with electrons. Figure 2 shows the type of reaction vessel used in the final experiments. It was designed to meet the following requirements: (1) to fit in a quart Dewar vessel; (2) to facilitate the conduction of heat away from the potassium chlorate; (3) to have the major portion immersed in liquid air with only the seals above the liquid air level. In order to meet the second of these requirements a mercury plate was substituted for the solid metallic plate.



A, Soft iron plunger; B, side tube for potassiun chlorate; C, drawn out tip to be broken by plunger; D, brass rod which stops the plunger; E, to accelerating voltage; F, filament leads; G, filament; H, mercury plate; J, mercury filler; K, Dewar flask with liquid air; L, liquid-air level.

Fig. 2.—Diagram of reaction vessel.

The entire apparatus, including the ionization gage, was first outgassed in a furnace heated to about 500° for eight hours. The part of the line not included in the furnace was kept hot by a hand torch. The liquid-air traps were then surrounded by liquid air and the filaments lighted. The plate and grid of the ionization gage were outgassed by bombardment with electrons accelerated through a potential of **10,000** volts. This treatment lasted for three hours. This prolonged outgassing not only removed adsorbed gases and vapor, but also the tungsten oxide coating sometimes formed on the inside of the ionization gage during the early stages of the outgassing.

After the outgassing the reaction vessel was cooled in a salt–ice bath and the mercury distilled into it. The reaction vessel was then immersed in liquid air and the solid mercury plate subjected to electron bombardment. No change in pressure was recorded by the ionization gage after a long interval. The entire process was repeated until no change in pressure was observed on standing for a twenty-four hour period.

The potassium chlorate (which had been kept in a vacuum desiccator over phosphorus pentoxide for six months) was now introduced into Tube B (Fig. 2) and sealed off. The weight A was raised by an electromagnet and allowed to drop. The weight was prevented from falling into the reaction vessel by the catch D. In this manner the potassium chlorate and a small amount of air were admitted to the reactionvessel while the vacuum pumps were running. The line was evacuated with the liquid air removed from around the reaction vessel and allowed to stand for twelve hours. A final evacuation was made before an experiment was started.

The mercury, H, was then given a negative potential with respect to the filament G and the filament lighted until an equilibrium condition was obtained, i. e., until there was no further diffusion of traces of air from the ionization gage to the reaction vessel or vice versa. During this time the reaction vessel was surrounded by liquid air. The mercury was now raised in the cut-off, C (Fig. 1), and the electrons were accelerated toward the potassium chlorate in the reaction vessel with a definite voltage. The two traps, D, were, of course, immersed in liquid air. The liquid air was continually replenished around the reaction vessel and the traps to keep conditions as nearly constant as possible.

Due to the gradual change of the storage batteries and to vibration in the building, there was a continual drift in the current through the ionization gage which could not be ascribed to a change in pressure. Accordingly, after one and three-fourth hours, the positive-ion current through the ionization gage was determined at two-minute intervals for fifteen minutes and then the mercury in the cut-off, C, was lowered and readings again taken at two-minute intervals. Any gas admitted to the ionization gage from the reaction vessel at this time would cause a change in the slope of the current–time curve. By this method a change in pressure of 10^{-8} cm. should be detectable.

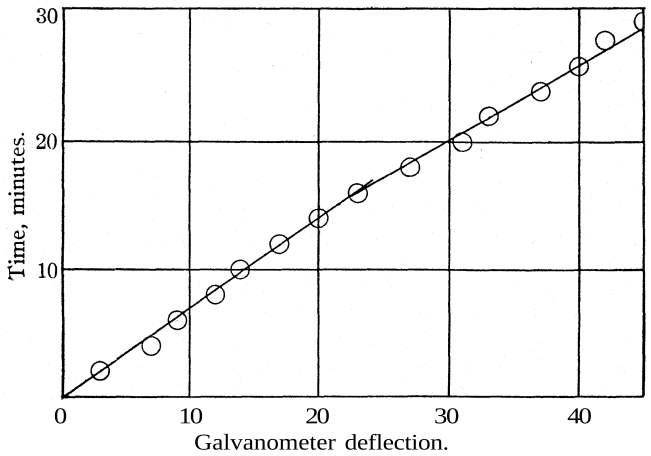


Fig. 3.

Figure 3 shows one typical curve when the accelerating voltage in the reaction vessel was 22 volts. There is a change in slope in the middle of the curve which indicates quite definitely that there was a real decomposition of the potassium chlorate brought about at this voltage. Curves at lower potentials showed no breaks which could be ascribed definitely to an increase in pressure. The experimental error in the determination of the minimum voltage is quite large.

There are two complicating factors which might make the detection of any reaction by this method difficult. The first of these is the adsorption of oxygen by the walls of the apparatus at liquid-air temperatures. This problem has been investigated by Langmuir.[8] He developed the equation $Q = abp/(1 + ap)$, where Q is the quantity of gas adsorbed in $mm.^3$ (measured at standard conditions) per $cm.^2$ of surface, a is a constant, 0.079, b is a constant, 8.46 and p is the pressure in dynes per $cm.^2$ This equation is not valid at very low pressures, but may be used to determine the order of magnitude of the adsorption. It can be shown that

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[8] Langmuir, THIS JOURNAL, 40, 1361 (1918).

if the surface at liquid-air temperatures is 200 cm.^{2}, the volume 1 liter and the bombarding current 10^{-8} amp., the decomposition should be detectable on the ionization gage without any difficulty if one electron causes the formation of one gas molecule. The second factor is the chemical clean-up. This matter has been discussed by Dushman.[9] Since the maximum pressure to be expected if one molecule of oxygen is liberated per electron passing through the reaction vessel is 10^{-5} cm., the chemical clean-up would undoubtedly reduce the pressure just about to the limit detectable by the ionization gage.

In view of these considerations it seems probable that detection of the decomposition would be difficult and would not be decisive unless a short chain reaction (say 10 to 100 molecules in length) were initiated by the electron bombardment. The only curves which showed any definite break were at accelerating potentials of 22 volts. This may possibly be ascribable to the slightly greater current at this potential.

(b) The Photochemical Decomposition.—Preliminary work on the photochemical decomposition of solid potassium chlorate was carried out with various glasses as color filters. It was found at first that there was an apparent photochemical decomposition brought about by radiation transmitted by soft glass unless the potassium chlorate was separated from the evacuating pumps and McLeod gage by a trap immersed in carbon dioxide snow and ether. Whether this means that there is some secondary reaction between potassium chlorate and mercury vapor was not investigated. When mercury vapor was removed, it was found that no decomposition could be produced by radiation from either a carbon or an iron arc except through quartz itself. All of the color filters excluded the active radiation. The solid was prevented from warming up by immersion of the reaction vessel in water. The pressure changes were measured by a quartz fiber manometer.[10]

The final measurements were made with a constricted arc[11] and a monochromatic illuminator with quartz prisms and lenses. The potassium chlorate was dried at a temperature of 105° for several days under a high vacuum and during illumination mercury vapor was excluded by a trap immersed in liquid air. The liquid air was removed from the trap in making the pressure reading.

With the monochromatic illuminator set at 313mμ no decomposition was observed, whereas decomposition was observed with the setting at 253mμ. The purity of the radiation was tested by photographing the spectrum with a quartz spectrograph. With the setting at 313mμ, lines down to 280mμ were faintly visible and with the setting at 253mμ lines

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[9] Dushman, *Gen. Elec. Rev.*, 24, 440 (1921).

[10] Haber and Kerschbaum, *Z. Elektrochem.*, 20,296 (1914).

[11] Forbes and Harrison, THIS JOURNAL, 47,2449 (1925).

up to 290mμ were detectable. No setting of the illuminator which completely excluded the 253.7mμ line of mercury caused any observable decomposition.

As a result of these experiments, it would seem that photochemical decomposition of potassium chlorate to give oxygen may be brought about by radiation of wave length below 280mμ. It would not seem possible to make any more accurate determination of the photochemical threshhold than this. The line at 313mμ is much more intense than the line at 253.7mμ. The lines in between are relatively weak in intensity.[11]

The quantum efficiency is of the order of 1/100 at 253.7mμ, neglecting radiation scattered by the solid.

II. Discussion of Results and Conclusions

The wave length required to produce photochemical decomposition of solid potassium chlorate is found to correspond to about 4.5 to 5.0 volts. The experiments on the electronic decomposition indicate that electrons of this kinetic energy do not cause a rapid decomposition of the potassium chlorate. The fact that from 10 to 100 molecules would have to decompose per electron to be conclusive would make any definite decision on this point impossible. There is the further difficulty in dealing with an insulating solid that the surface might well acquire a charge which would reduce the kinetic energy of the electrons below the threshold value. However, any decomposition at 20 volts would lead to the production of ionization in the gas phase, a fact which would lead to a partial dissipation of the surface charge as well as superimposing a photochemical on the electronic decomposition. It would seem entirely probable, therefore, that even with a decomposition of one molecule per electron at this high voltage, the resulting amplification would have made the effect detectable.

The possibility of increasing the rotation of a diatomic molecule to such a point that dissociation results is negligible, for the selection principle makes changes in rotational quantum number by ±1 only possible. Molecules may be dissociated, however, by increasing the vibrational quantum number beyond the convergence limit. For certain types of molecule this may be accomplished directly by the absorption of radiation. Dissociation may be produced by increasing the vibrational quantum number to such a point that change in electron level becomes possible. Dissociation of the excited molecule results if it possesses the requisite amount of energy. Thus hydrogen should be dissociated by energy corresponding to 4.46 volts[12] but radiation of this wave length is not absorbed by H_2 molecules and inelastic collisions of electrons in hydrogen are not observed at this voltage. However, it is possible to dissociate hydrogen

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[12] Richardson and Davidson, *Proc.* Roy. *Soc. London,* **123A, 466** (1929).

by wave lengths below 90mμ with the production of one normal atom and one atom in a two quantum state.

If a molecule is to be dissociated by electron impact, it may happen that an energy greater than that theoretically necessary for dissociation would be required. That is, to change the electron level without change in vibrational quantum number it may be necessary to add energy greater that that necessary to bring the molecule in the new electron state to dissociation. Hence the voltage required for dissociation may not agree with that calculated from spectroscopy, for there seem to be few if any cases on record where vibrational quantum number is changed by electron impact without accompanying change in electron level. In most cases the difference is not very great. For these reasons we see that it may not necessarily be possible to calculate the wave length required for photochemical decomposition from the kinetic energy of the electron which will produce the change and *vice versa*. Thus the simple relationship $eV = hc/\lambda$ (e is the charge on the electron, V is the accelerating voltage, h is Planck's constant, c is the speed of light and λ is the wave length) may not hold for the types of process referred to. In so far as conclusions are justified from these experiments, it would seem that there is lack of agreement between the two phenomena for solid potassium chlorate and that the activating processes are probably different.

The phenomenon of pre-dissociation[13] may be of importance in the photochemical decomposition of solids. That is, when the electron level is changed, the molecule may be in such a vibration state that change to another electron level becomes possible with resultant dissociation. For complicated molecules this type of process may easily occur. A diffuseness of the absorption bands is an indication of this phenomenon. Little quantitative work on the absorption spectra of solids has been done which would permit conclusions to be drawn on this point, although it is true that sharp absorption lines are not usually observed.

Summary

1. An attempt has been made to study the decomposition of solid potassium chlorate by bombardment with slow electrons. The results indicate that decomposition may be brought about by 22-volt electrons. Results with lower voltages are somewhat inconclusive but are, on the whole, negative.

2. Oxygen is evolved from solid potassium chlorate by the action of radiation of wave length shorter than about 280mμ.

3. A brief theoretical discussion is given.

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[13] Henri and Teves, *Nature*, **114**, 894 (1924).

[CONTRIBUTION FROM THE DIVISION OF PHYSICAL METALLURGY, NAVAL RESEARCH LABORATORY]

ABSOLUTE COHESION IN METALS. DISRUPTIVE NEGATIVE PRESSURES AND CRITICAL DISRUPTIVE VOLUMES[1]

BY ROBERT FRANKLIN MEHL

RECEIVED AUGUST 16, 1929 PUBLISHED FEBRUARY 6, 1930

The work of A. F. Joffe[2] has served to demonstrate that the tensile strength of crystals of sodium chloride as measured in air may be very greatly increased by the solvent action of water operating on the crystals during the tensile test (from 0.44 kg./mm.^{2} to 160 kg./mm.^{2}) and that this higher tensile strength indeed approaches the theoretical tensile strength (200 kg./mm.^{2}) as calculated by Zwicky[3] by an extension of the Born lattice dynamics.

Zwicky's calculation was based on the "theory of heteropolar crystals as developed by Madelung, Kossel, Born and others." It gives a negative pressure exerted in one dimension only, that is, as in the case of two separating plane surfaces, and is in qualitative agreement for sodium chloride with the calculation performed by Polanyi[4] making use of values for surface energy computed by the use of the lattice theory of Born. Joffe[5] has carried out a somewhat similar calculation which yields a negative pressure exerted in three dimensions, a quantity which likewise may be taken as a measure of absolute cohesion. The calculation of this maximum negative pressure is carried out in the following way. Born's well-known lattice energy equation is

$$U = -\frac{A}{r^m} + \frac{B}{r^n} \tag{1}$$

where U is the energy, A and B are constants, r is the interatomic distance defined as the cube root of the atomic volume divided by Avogadro's number. The first term represents the attractive potential and the second term the repulsive, with the condition that $n \gg m$. At the normal (zero external pressure) distance r_0, $\partial U/\partial r = 0$, that is, the force is zero. At any other distance we have

$$\frac{\partial U}{\partial r} = f = \frac{mA}{r^{m+1}} - \frac{nB}{r^{n+1}} \tag{2}$$

The terms for attraction and repulsion, mA/r^{m+1}, and $-nB/r^{n+1}$, respectively, may be plotted against r, as Joffe has done.[6] This gives a

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[1] Published by permission of the Navy Department, Washington, D. C.

[2] Summarized sufficiently for the present purpose in his book, "The Physics of Crystals," McGraw-Hill Book Company, New York, 1928.

[3] Zwicky, *Physik.* Z., 24, 131–137 (1923).

[4] Polanyi, Z. *Physik*, 1, 323 (1921).

[5] Ref. *2*, p. 21.

[6] Ref. *2*, p. 16. The terms of potential in Equation 1 can be plotted in a similar way. It is to be noted, however, that Joffe's diagram for potentials is incorrect, since it shows the energy curve passing through zero at $r = r_0$, whereas at equilibrium the potential is not zero but a minimum.

set of curves similar to those given in Fig. 1, where $\pi/V^{n'}$ is to be compared with mA/r^{m+1} and $-\pi/V^{m}$ with $-nB/r^{n+1}$, and where V replaces r. Since we have the condition n $\gg$ m, upon expansion (increasing r) the force reaches a maximum negative value and thereafter approaches the r-axis asymptotically. This maximum negative value of the force corresponds to a maximum possible expansion of the crystal, beyond which it will disrupt. Transferring into terms of pressures ($p = -\partial U/\partial V$; $\partial p/\partial V = -\partial^2 U/\partial V^2$) and making use of Equation 2 we may

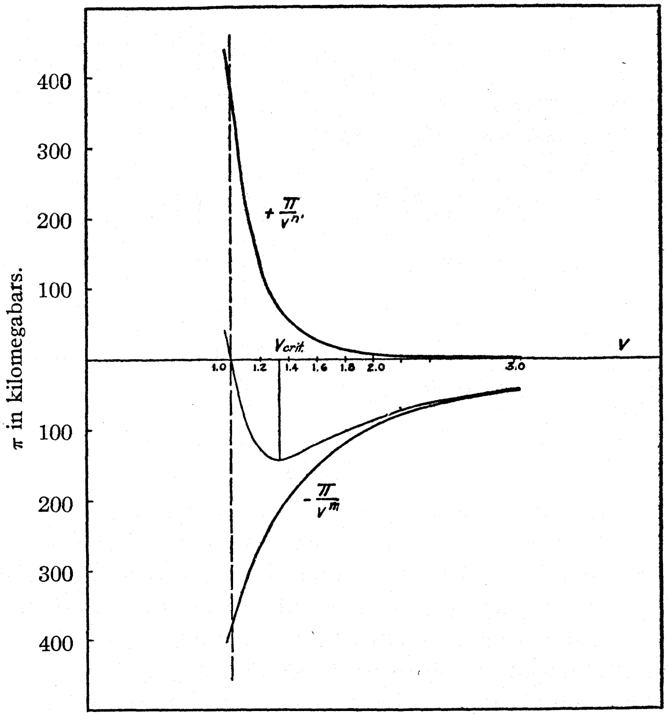

Fig. 1.—Internal **pressure–volume curves** for **copper.**

calculate the value of r at which the crystal will disrupt. Using this value the maximum negative pressure may be computed.[5] For sodium chloride this value is 350 kg./mm.[2]

This method has not been applied with success to metals, largely because of difficulty with the exponents m and n, and also because of the uncertainty in the application to metals of the conceptions underlying Equation 1, which is intended to treat of point charges in definite and known positions. It is the purpose of this paper to point out that the negative pressures necessary for disruption—disruptive negative pressures—may be calculated from the equation of state for solids developed by the late T. W. Richards.[7]

$$p + \pi_0 \left(\frac{V_0}{V_1}\right)^m = \pi_{\rho_0} \left(\frac{V_0}{V_1}\right)^n + P_\theta \tag{3}$$

in which p represent the external (atmospheric) pressure, $\pi_0(V_0/V_1)^m$ the internal cohesive pressure, $\pi_{\rho_0}(V_0/V_1)^n$ the internal expansive pressure, P_θ the internal expansive pressure caused by thermal agitation, V_0 the volume at p_0, and V_1 the volume at p_1. In this case also $n \gg m$.

For convenience in mathematical treatment this equation may be condensed[8] to

$$p + \pi_0 \left(\frac{V_0}{V_1}\right)^m = (\pi_{\rho_0} + P_\theta) \left(\frac{V_0}{V_1}\right)^{n'} \tag{4}$$

With zero external pressure $\pi_0 = \pi_{\rho_0} + P_\theta$, since $V_0 = V_1$. π_0 and $\pi_{\rho_0} + P_\theta$ are thus constant and equal.

Rewriting (4) we have

$$p = -\pi_0 \left(\frac{V_0}{V_1}\right)^m + (\pi_{\rho_0} + P_\theta) \left(\frac{V_0}{V_1}\right)^{n'} \tag{5}$$

Setting $V_0 = 1$ and $\pi_0 = (\pi_\rho + P_\theta) = \pi$, we have

$$p = -\frac{\pi}{V^m} + \frac{\pi}{V^{n'}} \tag{6}$$

The condition that p passes through a maximum (negative) pressure, which Equation 6 demands, is $\partial p/\partial V = 0$. Differentiating (6) with respect to volume we may solve for V

$$V = V_{\text{critical}} = \left(\frac{n'}{m}\right)^{1/(n' - m)} \tag{7}$$

This gives, then, the value for V at which the pressure passes through a maximum, in terms of the coefficients m and n, and is, therefore, the critical disruptive volume. In order to obtain the corresponding value for the disruptive negative pressure we may substitute this value in Equation 6 with the introduction of known values for m, n', π_0 and $\pi_{\rho_0} + P_\theta$, and solve for p, which may then be designated $p_{\text{max.}}$.

This formal treatment of Richards' equation of state, then, gives values for $p_{\text{max.}}$ and V_{critical} in a manner wholly analogous to the treatment of Born's equation as performed by Joffe. With the values of the coefficients m and n' and of the internal pressures calculated for the pure metals by Richards, it is, therefore, possible to obtain approximate values for the disruptive negative pressures and the critical disruptive volumes in metals.

It should be immediately remarked that both the method given here and that of Joffe can be regarded as only approximate because of the fact

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[7] Richards' paper in *Chem. Rev.*, 2, 315 (1925), is a good summary of his work and contains a complete bibliography, and together with his most recent paper on the subject, THIS JOURNAL, 48, 3063 (1926), may be regarded as sufficient reference to the many papers he published in this field.

[8] Richards, *ibid.*, 48, 3065 (1926).

that the constants in both cases are calculated from quantities measured at one atmosphere pressure or over a small range of pressures (up to only 10,000 kg./cm.^{2} in favorable cases). In addition, in the present case Equation 3 has been condensed into Equation 4, which may cause inaccuracies in higher ranges of pressures.[9] But admitting no great exactness in the final values, it is thought sufficiently interesting to make such calculations for the pure metals. At worst the present method suffers only those defects inherent in Joffe's method.

A comparison between the method proposed here and that given by Joffe may be carried out in the following way. π can be calculated for sodium chloride by the use of Richards' later and more accurate expression[10]

$$\pi = \frac{n'}{n' - m}\,\frac{R}{V_A\alpha_S} \qquad (8)$$

where R is the gas constant, V_A the atomic volume, and α_S the volume coefficient of thermal expansion. Richards has not calculated the exponents m and n' for sodium chloride, but these may be borrowed from Born after suitable transformation.[11]

Taking $\mathbf{m} = 1$ and $\mathbf{n} = 9$, we find m to be 4/3 and n' 4. Using these calculated values for m and n' we can calculate the internal pressure π (which Richards designated π_0), as in Equation 3

$$\pi = \frac{n'}{n' - m}\,\frac{R}{V_A\alpha_S} = \frac{4}{4 - \frac{4}{3}} \times \frac{(83.16 \times 10^6)}{13.53 \times 115 \times 10^{-6}} \times 10^{-6} = 80{,}000 \text{ megabars}$$

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[9] It should be noted in passing, however, that T. W. Richards (*J. Franklin Inst.*, *July*, 1924, *p*. 23) has shown that the heat of vaporization of mercury can be calculated by integrating the surface enclosed by internal pressure curves calculated from $m = 1.7$ and $n = 9.8$ with remarkable accuracy, the calculated and observed values being 55 kilojoules and 56 kilojoules, respectively. This calculation depends upon the extension of the range of applicability of the exponents to volumes (V_1) of five to ten times the original volume (V_0).

[10] Richards, THIS JOURNAL, 48,3067 (1926).

[11] I am indebted to Dr. R. H. Canfield of the staff of the Laboratory for the following transformation of exponents

$$p = \frac{\partial U}{\partial V} = \frac{\partial U}{3r^2\partial r} = -\pi\left(\frac{V_0}{r^3}\right)^m + (\pi_{\rho_0} + P_\theta)\left(\frac{V_0}{r^3}\right)^{n'}$$

$$\frac{\partial U}{\partial r} = -\frac{3\pi_0 V_0^m}{r^{3m-2}} + \frac{3(\pi_{\rho_0} + P_\theta)V_0^{n'}}{r^{3n'-2}}$$

$$U = -\frac{1}{1-m}\,\frac{\pi_0 V_0^m}{r^{3m-3}} + \frac{1}{1-n}\,\frac{(\pi_{\rho_0} + P_\theta)V_0^{n'}}{r^{3n'-3}}$$

$$= -\frac{A}{r^{\mathbf{m}}} + \frac{B}{r^{\mathbf{n}}}$$

$$\mathbf{m} = 3m - 3 \qquad m = \frac{\mathbf{m}}{3} + 1$$

Therefore

$$\mathbf{n} = 3n' - 3 \qquad n' = \frac{\mathbf{n}}{3} + 1$$

and also the critical disruptive volume, through Equation 7. The value obtained for the critical disruptive volume $V_{\text{critical}} = 1.52$, is, of course, identical with Joffe's value of $r_{\text{max.}} = 1.15$ ($r^3_{\text{max.}} = 1.52$), since the calculations of V_{critical} and $r_{\text{max.}}$ depend only upon the exponents which with the necessary transformation are identical in the two cases.

Introducing values for m, n', a and V_{critical} into Equation 6, $p_{\text{max.}}$ may be calculated and found to be 31,000 megabars. Converting this to kilograms per sq. mm. we obtain

$$p_{\text{max.}} = 316 \text{ kg./mm.}^2$$

which checks fairly closely with Joffe's value of 350 kg./mm.^{2}

This calculation, it is obvious, merely indicates that Richards' calculation of internal pressure gives a quantity which, after suitable transformation, is in definite agreement for sodium chloride with the constants in Born's equation. It must be taken as additional confirming evidence for the validity of Richards' equation.

It seems permissible, therefore, to carry out the calculation of disruptive negative pressures and critical disruptive volumes as outlined above for the metals, using the values for m, n' and π as given by Richards in one of his last papers.[12] From these values V_{critical} can be calculated by Equation 7, and with this $p_{\text{max.}}$ from Equation 6. The values thus obtained are listed in Table I.

These disruptive negative pressures may be taken as a measure of absolute cohesion. The conversion of this three-dimensional loading for metals to a one-dimensional loading seems impossible. Obviously it would be interesting to compare such a calculated tensile strength with the values for actual tensile strength. It is, however, by no means certain that a conversion of this sort would give a value strictly comparable to tensile strength values. It seems certain that the stress distribution in a breaking metal can by no means be represented as that occurring in two plane surfaces simply separated, but that there is a condition obtaining closely similar to the three-dimensional loading considered in the calculation above.[13]

Whatever might be the outcome of a calculation converting these disruptive negative pressures into true or absolute tensile strengths, it seems probable that the true or absolute tensile strengths would not be far from the calculated disruptive negative pressures, certainly of the same order of magnitude. Nothing further or more definite, however, can be said on this point.

Table I lists the tensile strengths of the pure metals corrected for reduction in area. It should be noted, however, that the reduction in area is always calculated from the area after fracture, which is usually less

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[12] Richards, THIS JOURNAL, 48, 3063 (1926).

[13] B. P. Haigh, *Proc. Int. Cong. App. Mech.*, Delft, 1924, p. 328.

than the area which bears the maximum load. In other words, the values for the reduction in area are rather too large, making the corrected tensile strength somewhat too great. The literature is surprisingly deficient in trustworthy data on the tensile strength of pure metals and even more so in data on reduction in area, so that the figures given must be regarded as approximate except for the common metals such as copper, iron and aluminum.

TABLE I

DISRUPTIVE NEGATIVE PRESSURES AND CRITICAL DISRUPTIVE VOLUMES IN METALS, WITH OTHER RELATED DATA AT 30°

(m = 2.00 throughout)

	n'	π, Kilo-megahars	V_{critical}	$p_{\text{max.}}$ kg/mm.^{2}	p_{max} lbs/in.^{2}	Ultimate tensile strength corrected, kg/mm^2	Ultimate tensile strength[a] corrected lbs./in.^{2}
Lead	7.75	72	1 27	340	322,000	2.1	3,000**
Aluminum	5 85	191	1.32	734	694,000	120.0	170,000*
Silver	6.76	208	1.29	896	848,000	32.4	46,000**
Gold	9.10	243	1.24	1,262	1,195,000	(26.0)	(37,000)**
Copper	5.64	376	1 33	1,399	1,325,000	133.5	190,000**
Palladium	6.76	396	1.29	1,705	1,614,000	(38.0)	(54,000)*
Tantalum	6.49	455	1.30	1,900	1,801,000	(93.0)	(132,000)*
Platinum	7.81	465	1.26	2,210	2,090,000	(37.3)	(53,000)**
Nickel	5.65	508	1 33	1,890	1,792,000	126	180,000*
Cobalt	5.56	510	1.33	1,870	1,772,000	85.0	121,000*
Iron	4 84	587	1 305	1,884	1,781,000	120	170,000*
Tungsten	5.27	1020	1.35	3,570	3,379,000	1190	1,700,000**

[a] The numbers in parentheses in the last two columns are uncorrected for reduction in area, no data being available. Those with the single star are from "International Critical Tables," Vol. II; those with a double star are from the Bureau of Standards Circular No. 101, "Physical Properties of Material," 1924. The tensile strength values chosen were always the highest found for metals of high purity.

It may be seen immediately that the corrected tensile strength data are very much lower than the calculated disruptive negative pressures, even allowing for a factor of conversion. The explanation which Joffe[14] gives for the low tensile strength of sodium chloride crystals in air, namely, the presence of cracks inducing stress concentrations and a resultant low tensile strength, is directly applicable to the case of metals. In fact, the importance of very fine cracks in the behavior of metals is now becoming generally appreciated throughout metallurgical literature. It is not impossible that the surface of most metals should be cracked in an ultra-microscopic fashion, as indeed Kapitza[15] has demonstrated for bismuth. In addition, the phenomenon of slip which generally attends

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[14] Ref. 2, pp. 56-66.

[15] Kapitza, *Proc. Roy. Soc. London*, *119*, 358 (1928); *cf.* Zwicky, *Proc. Nat. Acad. Sci.*, *15*, 253 (1929).

the failure of metals and alloys in the tensile test is conducive to the formation of a roughened surface (easily visible to the naked eye) through the sliding of crystalline blocks, producing reentrant angles on the surface of the test piece with accompanying concentration of stress. Such a stress concentration should lead to the formation of cracks, with a resulting observed tensile strength much lower than that possible through the complete elimination of cracks. Any condition imposed upon the metal to make slip more difficult should, therefore, increase the tensile strength. In a completely isomorphous series of solid solutions the tensile strength is much greater than the calculated rule of mixtures value, as is the hardness. It does not seem likely that the forces of cohesion are much affected by the solid solution formation,[16] so that it is possible that the recognized increased resistance to slip originating in lattice distortion should restrain the tendency for the formation of cracks through slip. The improvement in tensile strength of alloy steels and of the "age-hardening" alloys by heat treatment may then be regarded as caused partly or perhaps wholly by improved resistance to slip.[17] The high absolute cohesion as indicated by $p_{\text{max.}}$ therefore, suggests that alloys have by no means reached their maximum possible values of tensile strength, and that a complete knowledge of the ultramicroscopic cracks and of the phenomenon of slip might lead to the development of extremeiy strong alloys.

Summary

1. It is pointed out that Richards' equation of state for solids can be used in the calculation of the negative pressures necessary for the disruption of metallic lattices and of the critical volumes at which the disruption should take place, a calculation not hitherto performed.

2. With exponents borrowed from Born after suitable transformation the method yields a disruptive negative pressure for sodium chloride in agreement with that which Joffe calculated from Born's potential energy equation.

3. Disruptive negative pressures and critical disruptive volumes are calculated for the twelve cubic metals for which Richards has given the constants in his equation of state.

4. The values of the disruptive negative pressures obtained suggest that the tensile strengths of metals and alloys have by no means reached their maximum possible values.

WASHINGTON, D. C.

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[16] R. F. Mehl, THIS JOURNAL, 50, **73** (1928).

[17] Other factors besides simple solid solution formation may be operative in this respect, such as the production of fine hard particles in the slip planes, inter- and intracrystalline strains, unstable solid solutions, etc.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SOUTH CAROLINA FOOD RESEARCH COMMISSION, AND THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, UNIVERSITY OF MINNESOTA MEDICAL SCHOOL]

THE DETERMINATION OF TRACES OF IODINE. III. IODINE IN MILK, BUTTER, OIL AND URINE[1]

BY J. F. McCLENDON, ROE E. REMINGTON, HARRY VON KOLNITZ AND REDDING RUFE

RECEIVED AUGUST 21, 1929 PUBLISHED FEBRUARY 6, 1930

In the first paper of this series[2] was described a combustion tube method for the destruction of organic matter in foodstuffs for the purpose of determining traces of iodine. This method has since been used by Reith,[3] Schwaibold,[4] and others, and is the only workable method which we have found for iodine estimation in some classes of organic material. The second paper[5] describes a method of introducing dried vegetables into the tube, and some improvements which experience has suggested in the manipulation. It also describes a method of low temperature ignition in a muffle which has been found reliable for root and leafy vegetables (with a loss of about 15%) and which materially simplifies and shortens the technique. This alternative method was checked on known quantities of iodine added to potatoes, and on dried thyroid added to potatoes, with very satisfactory results.[6] When applied to skim milk powder this method sometimes failed. The loss was evidently sometimes due to too high a temperature in the first heating or smoldering of the sample. Duplicate samples done by the same chemist would check very accurately. Sometimes another pair of duplicates of the same sample done by another chemist would check but not check with the first pair. The smoldering must be carefully watched so that no live coals appear at the surface, in order to prevent loss. This is especially true of evaporated urine residues, particularly if only calcium oxide is added as an alkali. In this case only about 80% of added iodide was recovered. The low temperature method depends on the presence of a great excess of alkali and is, therefore, best adapted to vegetables other than cereal grains. Loss of iodine in ashing other samples can be prevented only by large additions of alkali and, therefore, to a certain extent defeats the purpose of the method, which is the freeing of the iodide from any large amount of other substances. The

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[1] Aided by a grant from the Joint Committee, University of Minnesota and Mayo Foundation, and from the Committee on Therapeutic Research, Council on Pharmacy and Chemistry, American Medical Association.

[2] J. F. McClendon, THIS JOURNAL, 50,1093 (1928).

[3] J. F. Reith, "De Micro-jodiumbepaling in Natuurlijke Grondstoffen," Dissertation, Utrecht, 1929.

[4] S. Schwaibold, "New Method for Determining Iodine in Organic Substances," *Chem.-Ztg.*, **54,** 22 (1929).

[5] J. F. McClendon and Roe E. Remington, THIS JOURNAL, 51,394 (1929).

[6] R. E. Remington, F. B. Culp and H. von Kolnitz, *ibid.*, 51,2942 (1929).

low temperature ashing method is not applicable to whole milk, fatty seeds, nuts or fats and oils. The present contribution will, therefore, describe methods which have been found suitable for these products, and some additional improvements in the original procedure.

Method for Fat (Including Butterfat).—The fat is melted and, if necessary, filtered free from water and suspended impurities. It is then introduced into the bottle of a large atomizer or lacquer spray apparatus (New Way Spray Gun Co., Cleveland), and sprayed into a silica tube (1 inch bore, 2 feet long with elbow 1 foot long) by means of a current of oxygen. The general set-up (Fig. 1) is the same as described in the preceding paper with some exceptions. It is necessary that the silica tube be very hot during the combustion or that a point in front of the atomizer be kept hot by means of a minute blast-flame or electrically heated platinum spiral. If electric heat is used outside the tube some provision for visibility should be made. A piece of platinum foil[7] or a platinum spiral of heavy wire in the tube acts as a catalyst. To close the end of the tube and prevent carbonization at the nozzle, it is surrounded with a pad of moist asbestos, which can be cooled by dropping water on it. The sodium hydroxide in the first wash bottle or absorption flask has been replaced by 0.25 g. of sodium sulfite, which insures that the iodine is reduced to the iodide form. In order to hasten the combustion, a rotary air pump drawing 2 cu. ft. of air per minute is used to suck the exhaust gases through the apparatus and ten Milligan wash bottles are used in parallel. It is necessary to cut the gas stream velocity down to a point where absorption is complete. All wash bottles are immersed in ice water. Following the wash bottles one or more towers packed with glass wool or an alundum extraction thimble to filter particles from the exhaust gases is inserted.

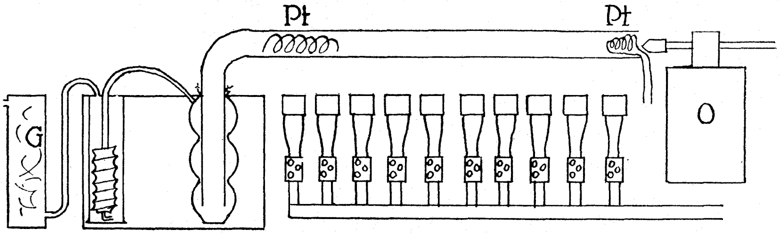

Fig. 1.—Combustion apparatus for burning fat and oil. The oil is placed in the container (O) of the atomizer and sprayed with oxygen into the silica tube, 2 feet long, 1 inch bore, with elbow 1 foot long. A platinum spiral (Pt) right in front of the atomizer tip is kept at white heat by means of an electric current. Another platinum spiral (Pt) further in the tube is heated by means of Meker burners under the tube. The elbow in the silica tube dips into an absorption flask of three compartments and the joint is packed with asbestos fiber. This is connected with ten Milligan wash-bottles in parallel, all immersed in ice water, which are connected with a tower packed with glass wool (G) and finally with an exhaust pump.

The adjustment of the atomizer is very important, for if the ratio of oxygen to fat is too high, the fatty acids will not burn, but will distil over. If, on the other hand, too little oxygen is used, soot will form. The atomizer is best adjusted in a preliminary

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[7] A tube lined with a platinum film soon cracked. A manganous salt added to the fat as a catalyst did not improve the combustion. Probably a rare earth salt would be useful.

trial and kept set during the combustion. The amount of fat burned is determined by weighing the atomizer bottle before and after the combustion. If the iodine content is low, it may be necessary to burn as much as 500 g. of fat. It is possible to so conduct the burning that no soot and tarry products are formed. The liquid in the wash bottles is placed in a beaker, the rinsings of the apparatus added, evaporated to small volume, transferred to a nickel boat, evaporated to dryness and ignited in a pyrex tube (Fig. 2), using about 5 cc. of water and a few milligrams of sodium sulfite in a side-necked test-tube to absorb volatilized iodine. If an alundum capsule is used it is ignited in the same tube. The boat is placed in the smallest test-tube into which it may be introduced, the sulfite solution added, together with rinsings of the tube, and left until the ash has dissolved. The solution is centrifuged free from insoluble residue, decanted into a 30-cc. beaker, a few drops of sulfurous acid (to reduce iodate) and a few milligrams of sodium azide added (to decompose nitrites) and neutralized with sirupy phosphoric acid, using bromphenol blue paper as indicator. Four drops of phosphoric acid are added in excess and the solution boiled to remove sulfur dioxide (as well as excess hydrazoic acid).

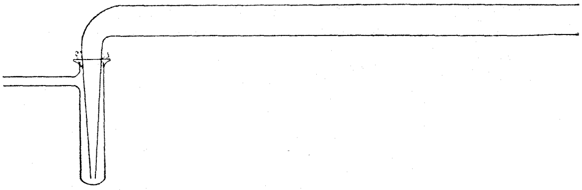

Fig. 2.—Small pyrex combustion tube and side-necked test-tube for absorbing iodine from the combustion.

If the odor of hydrazoic acid is not perceived, more sodium azide is added. It was shown by Reith that there might be considerable nitrite formed in the combustion of foodstuffs containing nitrogen, and that the nitrite might be decomposed by hydrazoic acid.

The solution is now transferred to a small separatory funnel with an etched mark at **10** cc., made up to the mark with distilled water and about 1 mg. of sodium nitrite added, followed by **1** cc. of purified carbon tetrachloride. The separatory funnel is shaken for at least two minutes, during which time the iodide is oxidized to iodine and 85/95 of the iodine passes into the carbon tetrachloride solution and is compared with a standard containing 0.1 mg. of iodine per cc. in a Bausch and Lomb micro-colorimeter. This is multiplied by 1.118 to correct for the partition coefficient of iodine between carbon tetrachloride and the dilute salt solution. Or, since this partition coefficient varies

TABLE I

IODINE CONTENT OF BUTTERFAT

Town	County	State	Iodine, parts per billion
......	.....	Minnesota	4.0
St. Paul	Ramsey	Minnesota	11.0
Orono	.....	Maine	13.0
Hasson	.....	Minnesota	14.3
......		Minnesota	15.7
Nelson and Wadena		Minnesota	16.5
Davis		California	26.3
Wadena		Minnesota	28.9
Charleston		South Carolina	52.7
Clemson College		South Carolina	78.0

slightly with variation of salt content, the solution may be repeatedly extracted with carbon tetrachloride and the yields of the different extractions added together.

By this method the iodine content of a sample of Norwegian cod-liver oil was found to be 5800 parts per billion.

Method for Oily Seeds and Nuts and Milk.—On account of the large amount of fat or protein present, low-temperature ignition is not successful on this class of products, even though one is content with 85% recovery, and since the material cannot be sprayed, the tube furnace with the screw feed is used. Visking sausage casing has been found very satisfactory as a lining in which to pack the dry material before introduction into the screw feed device. The mouth of the feed tube ($^7/_8$-inch bore) is brought into juxtaposition with the end of the silica tube furnace (1-inch bore) and oxygen delivered to the crack by a nozzle made from an ordinary flame spreader ("fish-tail" or "wing-top" for Bunsen burner) which has been bent into a curve to fit the outside of the feed tube (Fig. 3, the detail above the diagram shows the flame spreader from another angle).

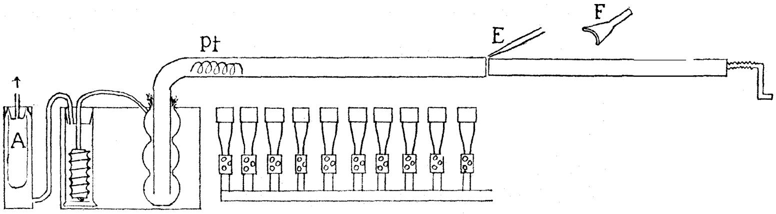

Fig. 3.—Combustion apparatus for burning solid food materials. The arrangement is the same as in Fig. 1, except that the atomizer is replaced by a steel tube of $^7/_8$-inch bore with a micrometer screw for forcing the foodstuff into the silica tube. The foodstuff is packed in a Visking sausage casing which is inserted in the steel tube. Oxygen is emitted through the adapter (E) which is shown at perspective at (F). The tower of glass wool shown in Fig. 1 is replaced by an alundum capsule (A) for straining out the particles of smoke that might escape the absorption flask.

About 6 inches of the silica tube is lined with sheet iron or nickel for protection from the ash. After igniting the material by means of a flame, the joint is covered with a lump of wet asbestos fiber and kept moist. The combustion is then carried on as previously described. The ash is ground for one hour with 100 cc. of 95% alcohol in a 250-cc. ball mill and then for one hour with 100 cc. of 80% alcohol; the combined extracts are centrifuged and the combined alcohol extracts decanted, evaporated and added to the evaporated washings of the apparatus. If a yellow or dark color appears, the residue must be transferred to a nickel boat and ignited in the small tube, Fig. 2.

Milk is best neutralized with sodium hydroxide, using phenol red paper as indicator, evaporated to small volume on a water-bath, some rare earth (ceria or thoria) and sulfur added, heated in an oven at 100° until dry, then ground in a burr mill or broken into pieces and packed in Visking sausage casing. The evaporation of milk in open dishes is tedious and wherever possible milk powder is obtained. The rare earth seems to act as a catalyst in combustion,[8] and the sulfur aids in the reduction of iodine.

Geographical surveys on the iodine content of milk are meaningless unless considerable data are collected, since it has been shown that the feeding of iodine compounds increases the iodine content of the milk, and there are now on the market many dairy feeds which contain fish

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[8] Personal communication of O S Rask.

meal, ground kelp and mineral iodides. The iodine content of whole milk may be calculated from the iodine content of butterfat and skim milk. We were able to determine the iodine content of the "hulls" of the fat droplets after feeding a cow iodide, but ordinarily we think this fraction is negligible.

Since butterfat is used for human consumption to a greater extent than are the other constituents of milk, it is of interest to know the ratio of the iodine in the butterfat to that in the skim milk of the same sample of milk. For this purpose about five gallons of milk are separated, the cream is churned and the total iodine content of the skim milk plus buttermilk determined separately from that of the butter.

TABLE II

DISTRIBUTION OF IODINE IN COW'S MILK

Town	County	State	Feed	Iodine in parts per billion Butterfat	Iodine in parts per billion Dry skim milk	Ratio of total iodine in butter to that in skim milk
Clemson College	.....	S. C.	Normal	78	142	0.9
Davis	.....	Cal.	Normal	26	164	04
Byron Rock River Farm	.....	Ill.	Kelp and fish	176	400	.7
St Paul[a]	Ramsey	Minn.	Normal	11	.....	...
St. Paul	Ramsey	Minn.	Cod-liver oil	36	7,320	.002
St. Paul	Ramsey	Minn.	Iodized oil,[b] 100 g. daily	43	65,600[c]	.0006
St. Paul	Ramsey	Minn.	Iodized salt containing 10% iodine	378	158,000	.0004
St Paul	Ramsey	Minn.	4–6 Days after discontinuing iodized salt	148	2,800	.02

[a] With cooperation of Dairy Division, Department of Agriculture, University of Minnesota.

[b] Made by adding 20 *g.* of ICl_3 to a gallon of linseed oil.

[c] Iodine in hulls, 26,000.

The above results of feeding a cow iodized salts equivalent to 10 g. of iodine a day for five days and another cow iodized oil are not in agreement with those of Scharrer and Schwaibold[9] or of Rasche.[10] It seems probable that these discrepancies are due to losses of iodine in analysis and we doubt whether accurate analyses can be made on samples much smaller than ours by any method.

Method for Urine.—If the urea is not destroyed it becomes troublesome to burn the urine residue because the decomposing urea forms gases which foam and sputter, causing loss and putting out the flame. The twenty-four hour urine specimen is colored with phenol red, neutralized

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[9] K. Scharrer and J. Schwaibold, "Über die Art der Bindung des Jods in der Milch," *Biochem.* Z., 207, 333 (1929).

[10] W. Rasche, *Z. Kinderheilkunde,* 42, 124 (1926).

with lime water and subjected to hydrolysis with urease (about 5 cc. of the extract of 5 g. of jack bean meal). An hour suffices for the hydrolysis of the urea, after which 5 g. of lime is added and the urine evaporated to a small volume. (The use of a hot-plate regulated at 100°, Fig. 4, avoids the danger of overheating.) When evaporated to small volume the urine is transferred to a nickel boat, some rare earth and sulfur added, evaporated to dryness and ignited in an excess of oxygen in a pyrex tube furnace (Fig. 5) by first heating the material nearest the absorption flask by means of an oxy-gas torch or electrically heated platinum loop and working back to the open end of the tube.

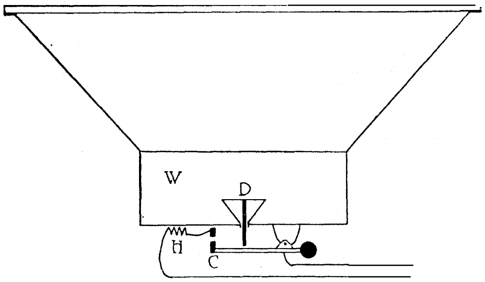

Fig. 4.—Constant temperature hot-plate, kept at 110" by means of an electric regulating apparatus. The hot-plate is the top of an evacuated chamber, the lower portion of which is filled with water (W) and heated by the electric heater (H). When the water (W) boils and produces steam above atmospheric pressure, the diaphragm (D) is pushed down, forcing down the electric contact (C) and thus breaking the circuit and cutting off the heat.

The pyrex tube furnace shown in Fig. 5 is reduced in size stepwise so as to accommodate nickel boats of different sizes. The platinum spiral is heated by the electric current from a transformer in which the voltage may be varied by turning a knob (Franklin Transformer Company, Minneapolis). It may be heated by means of a gas flame below the tube, but there is more danger of softening the pyrex. The spiral is heated so as to be luminous in a darkened room but not perceptibly luminous in a brightly lighted room. The oxy-gas torch has an opening made by driving a needle through the oxygen tube, thus directing a stream of oxygen forward so as to supply oxygen to the platinum spiral and complete the combustion of gases. The torch itself has the gas cut down to a small rate and the oxygen supplied in excess so that the heated urine residue will burn with a dazzling luminosity. In case an electrically heated platinum loop is substituted, an attached tube carries oxygen, which is directed toward the loop. The loop is plunged into the urine residue and moved slowly backward until all is ignited.

If any tarry film condenses on the pyrex tube it is burned off by placing a gas flame under it.

At the end of the combustion the ash has a light gray color or is almost white. The ash is ground for one hour in a 250-cc. ball mill with 100 cc. of 95% alcohol, followed by one hour with 100 cc. of 80% alcohol, and the combined extracts are centrifuged and decanted. The extracts, sulfite solution and washings of the tube are evaporated in a porcelain dish to a small volume and, if necessary, centrifuged again and transferred to a nickel boat, evaporated to dryness, and ignited in the smaller pyrex tube (Fig, 2). The analysis is then continued as in analysis of iodine in fat.

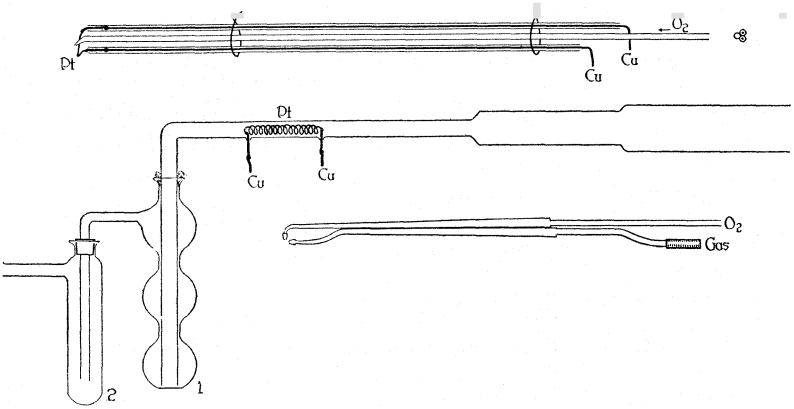

Fig. 5.—Apparatus for burning urine residue. The urine is placed in a nickel boat and is inserted into the pyrex tube which is narrowed stepwise. The boat is placed in the narrowest portion which will conveniently receive it. The platinum spiral (Pt) is heated by means of the copper connection (Cu) in the middle of the figure. The pyrex combustion tube is bent down into a tripartite absorption flask (1) and the joint closed with asbestos. The second absorption flask (2) is closed by means of a rubber stopper. Heat is supplied by means of the oxy-gas torch, shown below, with an extra opening in the oxygen tube, allowing oxygen to pass forward, or by means of the apparatus shown above. To show the details the binding wires are loosened so that the three parts are shown separately. The middle tube (O) carries oxygen, which is directed toward the platinum loop (Pt) and in each of the other tubes is a pyrex tube containing a copper wire, which is welded onto a large platinum wire, which, in turn, is connected onto the platinum loop of finer platinum wire (Pt), which is heated to a white heat by means of an electric current. The gas or electric torch is held in the hand and inserted inside the pyrex combustion tube in order to burn the urine residue.

In order to determine the behavior of the apparatus, relatively large quantities of iodide were added to small samples of iodine-free substances and burned in the tube. Ten mg. of iodine (as potassium iodide solution) was added to 50 cc. of iodine-free urine treated as above described, and burned in the tube. There was recovered

8.10 mg. in the ash in the boat
0.49 mg. in the washings of the tube
0.47 mg. in the 1st absorption tube
0.055 mg. in the 2nd absorption tube

Total, 9.115 mg. of iodine recovered

On repeating this experiment the following values were obtained

3.07 mg. in the ash in the boat
0.375 mg. in the washings of the tube
5.562 mg. in the 1st absorption tube
0.762 mg. in the 2nd absorption tube

Total, 9.769 mg. of iodine recovered

Ten mg. of iodine (as potassium iodide solution) was added to 5 g. of iodine-free starch and burned in the tube with the following recovery

7.94 mg. in ash in the boat
1.26 mg. in 1st absorption flask (none found in 2nd absorption flask)
0.13 mg. in washings of tube

Total, 9.33 mg. of iodine recovered

This experiment was repeated, with the following results

9.66 mg. in the ash in the boat
0.52 mg. in the 1st and 2nd absorption flasks
0.05 mg. in the washings of the tube

Total, 10.23 mg. of iodine recovered

The recovery was within the limits of accuracy of the pipet in which the iodide solution was measured. The variations in the distribution of iodine in different parts of the apparatus were probably due to variations in temperature, duration of heating and rate of suction of air and exhaust gases through the apparatus. If potassium iodide is heated in a test-tube over a Bunsen burner, elemental iodine is evolved. It is not necessary to raise the temperature sufficiently to sublime the iodide in order to carry over iodine into the absorption flasks. If there is not sufficient sulfite in the absorption flasks, iodine will color the solutions in them (and some be lost, passing into the suction pump), and the color disappears on adding more sulfite.

Eight (24-hour) urine specimens of Minnesota men who used ordinary non-iodized salt ranged between 0.008 and 0.011 mg. (av. 0.00956) of iodine. Nine (24-hour) urine specimens of Minnesota men who used iodized salt ranged from 0.068 to 0.295 (av. 0.1213 mg.). The great variability is probably due to variability of intake of iodine. The average iodized salt contains about 1.4 mg. of iodine per 100 *g.* of salt. The amount used by the subjects was not controlled. In two determinations on days following strenuous exercise, the iodine excreted in the urine was double that on other days, but the iodine intake was not investigated. In one determination day-urine contained about twice as much iodine as night-urine (12-hour day urine, 0.09, and 12-hour night urine, 0.05 mg. of iodine).

RESULTS OF ANALYSES

Subject	Mg. of iodine in 24-hour urine No iodized salt used	Subject	Mg. of iodine in 24-hour urine Iodized salt used
I	0 008	1	0.068
2	.008	2	.082
3	.009	3	.085
4	.0095	1	.102
5	01	4	.112
5	01	4	.128
2	011	1	.128
6	011	4	182
		I	.205[a]
Average	0.00956	Average	0 1214

[a] Way following heavy exercise.

Summary

1. Foodstuffs and urine are burned with oxygen in a silica or pyrex tube furnace, using an atomizer for oils and a screw feed device for solid substances. Heat is applied from the outside by gas burners or from the inside by electrically heated platinum wires or oxy-gas torches. Urine is freed from urea with urease and burned in a pyrex tube furnace.

2. Sodium sulfite solution is used to absorb the iodine, and hydrazoic acid to free it from excess nitrite. The iodide is oxidized with a known quantity of nitrite to iodine and shaken out with carbon tetrachloride.

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

THE HEAT CAPACITY AND ENTROPY OF POTASSIUM PERCHLORATE FROM 12 TO 298° ABSOLUTE. THE HEAT OF SOLUTION OF POTASSIUM PERCHLORATE. THE ENTROPY AND FREE ENERGY OF PERCHLORATE ION

BY WENDELL M. LATIMER AND J. ELSTON AHLBERG[1]

RECEIVED SEPTEMBER 3, 1929 PUBLISHED FEBRUARY 6, 1930

This work is a continuation of the program[1a] for the evaluation of entropies of aqueous ions and constitutes an example of the application of these values to the determination of the free energy of a negative ion which is not readily obtained by the ordinary equilibrium or electromotive-force methods.

The following measurements were made: (1) the heat capacity of po-

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[1] Du Pont Fellow in Chemistry.

[1a] For references to the general theory see (a) Latimer and Buffington, THIS JOURNAL, 49, 2297 (1927); (b) Latimer, *ibid.*, 48, 2868 (1926); (c) Latimer and Greensfelder, *ibid.*, 50, 2202 (1928); (d) Latimer and Kasper, *ibid.*, 51, 2293 (1929); (e) Latimer, *J. Phys Chem.*, 31, 1267 (1927).

tassium perchlorate from 12 to 298°K., (2) the heat of solution of potassium perchlorate at 208.1°K. These values have been used in the calculation of the entropy of potassium perchlorate and the entropy and free energy of perchlorate ion.

Material.—The potassium perchlorate used was Baker's "C. P.," which was recrystallized four times and dried for 100 hours under vacuum. Analysis indicated the purity to be at least 99.9%.

Measurement of Heat **Capacity.**—The experimental method follows the general plan used by Latimer and Greensfelder" and reference may be made to their paper for a description of the experimental technique. In cooling the calorimeter to the lowest temperature, ll.S°K., the three-stage vacuum pump described by Giauque and Johnston[2] was used. All runs were timed by a stop watch calibrated before and after measurements with watches at the University Observatory. The values obtained for the specific heat and the molal heat capacity are given in Table I in calories per degree K. The high value at 274.75°K. may be explained by the assumption of less than 0.1% of water occluded inside the crystals. The mean deviation of the values excluding the lowest and the ice points is ±0.3%.

TABLE I

HEAT CAPACITY PER GRAM AND PER MOLE OF POTASSIUM PERCHLORATE

Temp., °K.	C_p per gram	C_p per mole	Temp., °K.	C_p per gram	C_p per mole
12.53	0.00523	0.725	122.27	0.1238	17.15
16.39	.00763	1 058	132.15	.1273	17.64
19.49	.01217	1 686	142 22	.1311	18.17
21.85	.01622	2 247	153.21	.1355	18.77
23.98	,01981	2 745	163.78	.1402	19.43
27.02	02567	3 557	175.05	.1445	20.02
33 39	,03882	5.379	186 90	.1479	20.49
37.01	.04606	6.382	192 38	1502	20.81
45.18	060'38	8.366	202 90	.1544	21.39
54 79	07434	10 30	213.09	.1589	22.01
58.95	.07939	11.00	224 60	1631	22.60
62.99	.08384	11 62	230.85	.1632	22.61
66.58	.08726	12.09	237.33	.1663	23.04
71.74	09244	12.81	243.95	.1670	23.14
73.37	.0978	13.55	250.30	1700	23.50
80 63	.1004	13.91	256 32	.1719	23.86
89.53	.1063	14.73	262 58	.1756	24.33
90 37	.1066	14.77	268.90	.1888	26.16
94 40	1089	15.08	274 75	.1982	27.46
99 87	1118	15 49	280.46	1875	25 98
105 29	1141	15.80	286 33	.1869	25.90
110.16	.1172	16 23	291.49	.1864	25.82
117 13	.1210	16.76	298.07	.1901	26 34

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[2] Giauque and Johnston, THIS JOURNAL, 51, 2300 (1929).

Entropy of Potassium **Perchlorate.**—Figure 1 gives the plot of C_p against log T, from which the entropy may be obtained graphically as the integral $S = \int C_p \, d \ln T$. The extrapolation at low temperatures was carried out by fitting the lower points to a Debye function. In this region the curve is rapidly approaching the T^3 law. The value which we found from the integration is $S_{298.1} = 36.1 \pm 0.3$ cal./deg.

Heat of Solution.—The measurements of the heat of solution were made in a calorimeter which consisted of a vacuum-walled flask of about a liter capacity fitted with a stirrer and resistance thermometer. The resistance thermometer contained about 300 ohms of number 40 copper wire and served also as the heating coil for the determination of the heat capacity of the calorimeter. A small tube in the neck of the flask contained a definite weight of the solid potassium perchlorate, which could be dumped into the water by an outside control. The whole apparatus was submerged in a 25° thermostat constant to 0.01°. The value obtained for the heat of solution of one mole of potassium perchlorate in 1800 moles of water at 298.1°K. was 12,115 ± 30 cal.

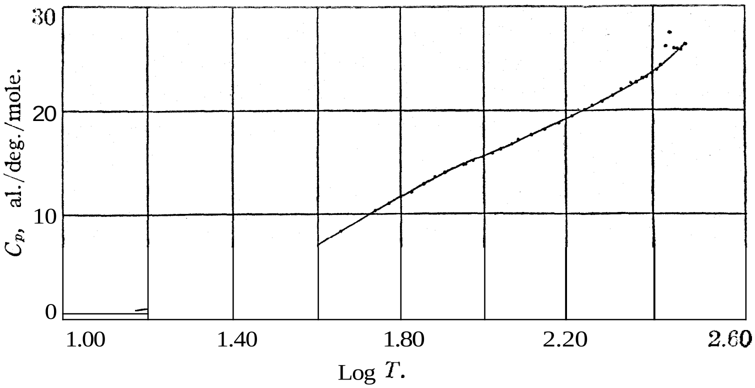

Fig. 1.—Molal heat capacity of potassium perchlorate.

Entropy of Perchlorate Ion.—We may now calculate the entropy change for the process: solid potassium perchlorate to give a hypothetical one molal solution of its ions, from the relations

$$\Delta S^\circ = \frac{AH - AF^\circ}{T} \quad \text{and} \quad \Delta F^\circ = -RT \ln (\gamma m)^2$$

This requires in addition to the heat of solution AH a knowledge of the solubility, m, and the activity coefficient, γ. The former has been carefully determined by a number of investigators;[3] their results, agreeing

[3] (a) Noyes, Boggs, Farrell and Stewart, THIS JOURNAL, 33, 1650 (1911); (b) Noyes and Sammet, *Z. physik. Chem.*, 43, 534 (1903); (c) Rothmund, *Z. physik. Chem.*, **69**, 538 (1909).

to within 0.3%, give $m = 0.148$ mole per liter at 298.1°K. The activity coefficient in the saturated solution is not readily determined experimentally, as the ordinary freezing-point method encounters as a difficulty the small solubility of the salt at low temperatures. From the conductivity measurements of Noyes and Sammet,[3b] the value α_λ for the saturated solution at 298.1°K. is 0.78, and since this value agrees closely with the value for potassium nitrate, we feel justified in assuming the activity coefficient as given by Lewis and Randall[4] for the latter salt, namely 0.70 ± 0.05. This then gives

$$\Delta F^\circ_{298}, = -1364\ 9 \log (0.148 \times 0.70)' = +2690 \pm 100 \text{ cal.}$$

and

$$\Delta S^\circ_{298}, = \frac{12{,}115 - 2690}{298.1} = +31 \text{ ti entropy units}$$

Using our value for the entropy of the solid, 36.1, we obtain for the sum of the entropies of potassium and perchlorate ions, 67.7. Latimer and Buffington gave 22.0 for the entropy of potassium ion as the average of two methods. This now becomes 21.5 when we use the recent value of Lange[5] for the heat of solution of potassium chloride which entered into one of the calculations. Hence we obtain for the entropy of perchlorate ion in the hypothetical one molal solution at 298.1°K, $S^\circ_{298.1} = 46.2$.

Free Energy of Perchlorate **Ion.**—Berthelot[6] found as the average of two methods for the reaction,

$$KClO_4 = KC1 + 202 \quad . \quad A\,H = +7600 \text{ cal.}$$

Combining this with our experimental heat of solution of potassium perchlorate and with Lange's value for the heat of solution at infinite diiution of potassium chloride, +4157 calories, we obtain

$$ClO_4^- = Cl^- + 2O_2 \qquad AH = -358 \text{ cal.}$$

Then from the value of the entropy of perchlorate ion obtained above, the entropy of chloride ion,[1b] 15.6, and the entropy of oxygen,[2] 49.03, we obtain for the same reaction, $\Delta S^\circ_{298.1} = 67.5$. Hence

$$ClO_4^- = Cl^- + 202 \qquad \Delta F^\circ_{298.1} = -358 - 298.1 \times 67.5$$
$$= -20{,}480 \text{ cal.}$$

We can also calculate, as a check, the free energy of this reaction by another path which does not involve the ionic entropies. Thus using the entropy of potassium chloride,?19.7, together with that for potassium perchlorate and oxygen, we obtain

$$KClO_4 = KCl + 2O_2 \qquad \Delta F^\circ_{298.1} = +7600 - 298.1 \times 81.7$$
$$= -16{,}755 \text{ cal.}$$

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[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Kill Book Co., New York, **1923.**

[5] Lange, *Z.* Elektrochem., 35, 29 (1929).

[6] Berthelot, *Ann. chim. phys.,* [5] **27,** 226 (1882).

[7] Lewis and Gibson, THIS JOURNAL, 39, 2554 (1917).

Combining this value with the free energy of solution of potassium perchlorate, +2688, and of potassium chloride,[8] −936, gives

$$ClO_4^- = Cl^- + 2O_2 \qquad \Delta F^\circ_{298.1} = -20{,}379 \text{ cal.}$$

Using −20,430, the average of the two methods, and the Lewis and Randall[4] value for the free energy of chloride ion, −31,367, we obtain for the *free energy of perchlorate ion*, $F^\circ_{298.1} = -10{,}937$ cal.

The error in this value is determined very largely by the accuracy of the heat of decomposition of potassium perchlorate measured by Berthelot. Although this is difficult to estimate, we judge it is within ±500 cal.

For many purposes it is more convenient to express the free energy of perchlorate ion in terms of the reduction potential referred to the H_2–H^+ couple as zero. Using the Lewis and Randall[4] value for the free energy of water, we find

$$\tfrac{1}{2}Cl_2 + 2H_2O = ClO_4^- + 8H^+ + 7E^-;\ E^\circ = -1.333 \pm 0.005$$

Summary

The specific heat–temperature curve and the heat of solution of potassium perchlorate have been determined. These values have been used in the calculation of the entropy and free energy of perchlorate ion.

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

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. XII. THE DETERMINATION OF TELLUROUS ACID

BY H. H. WILLARD AND PHILENA YOUNG

RECEIVED SEPTEMBER 5, 1929 PUBLISHED FEBRUARY 6, 1930

Introduction

An excellent survey of the volumetric methods proposed for tellurium up to the year 1926 has been given by Lenher.[1] The electrometric titration of tellurate with titanous chloride either in a hydrochloric or a sulfuric acid solution has been described recently.[2] The volumetric method based upon the oxidation of tellurous acid by dichromate, proposed first by Brauner[3] and modified by Moser and Miksch,[4] Lenher and Wakefield,[5] and Schrenk and Browning,[6] appears to be the most satisfactory and is applicable in the presence of selenious acid. The oxidation, if carried out at room temperature in hydrochloric acid solution,[5] is rather slow and

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[8] Rodebush, *ibid.*, 40, 1204 (1918).

[1] Lenher, *Proc. Am. Phil. Soc.*, 65, 33 (1926).

[2] Tomiček, *Bull. soc. chim.*, 41, 1389 (1927).

[3] Brauner, *Monatsh.*, 11, 526 (1890).

[4] Moser and Miksch, *ibid.*, 44, 349 (1923).

[5] Lenher and Wakefield, THIS JOURNAL, 45, 1423 (1923).

[6] Schrenk and Browning, *ibid.*, 48, 139 (1926).

the concentration of hydrochloric acid must be carefully controlled. If too low, the speed of the reaction is retarded; if too high, hydrochloric acid and telluric acid react to give free chlorine. Schrenk and Browning[6] carried out the oxidation at room temperature in a sulfuric acid solution, forty-five to sixty minutes being required for complete oxidation. They did not study the reaction in hot solution.

This paper describes a rapid and accurate volumetric procedure for tellurium, based upon the oxidation of tellurous acid by excess standard ceric sulfate in the presence of chromic sulfate as catalyst, and electrometric titration of the excess ceric sulfate with standard ferrous sulfate.

Experimental

The potassium tellurite solution was prepared by dissolving pure basic tellurium nitrate in dilute potassium hydroxide, and was approximately 0.09 N. It was standardized by the method of Lenher and Wakefield[5] against dichromate of known purity, the excess of dichromate being titrated electrometrically with ferrous sulfate. A 0.1 N selenious acid solution was prepared from high grade selenious acid. The ceric sulfate solution was a part of a large supply made by the method described by the authors[7] from high-grade ceric oxide and was 0.5 M in sulfuric acid. It was standardized against sodium oxalate.[8] The ferrous sulfate solution was standardized electrometrically against standard ceric sulfate.[8]

The oxidizing action of ceric sulfate on selenious acid and tellurous acid was first tested. Measured portions of 0.1 N selenious acid were diluted with water, 25 cc. of 0.09611 *N* ceric sulfate and sulfuric acid (sp. gr. 1.5) to 200 cc., heated to boiling, held just below the boiling point

TABLE I

THE OXIDIZING ACTION OF CERIC SULFATE ON SELENIOUS ACID

In each experiment 25 cc. of 0.09011 *N* ceric sulfate was added

0.1 N H_2SeO_3 cc.	H_2SO_4 (sp gr. 1.5) before ox, cc.	Time at b. p., min.	0.1 *N* $Ce(SO_4)_2$ reduced cc.
10	10	30	0.16
10	30	30	.04
10	50	30	.01
10	10	60	.42
10	30	60	.05
10	50	60	.03
25	10	30	.17
25	30	30	.03
25	50	30	.03

TABLE II

THE OXIDIZING ACTION OF CERIC SULFATE ON TELLUROUS ACID

In each experiment 25 cc. of 0.09611 *N* ceric sulfate was added

0.09 *N* K_2TeO_3, cc.	H_2SO_4 (sp gr. 1.5) before ox, cc.	Time at b. p, min.	0 1 N $Ce(SO_4)_2$ reduced, cc.
10	10	30	0.62
10	30	30	.44
10	50	30	.28
10	10	60	.74
10	30	60	.81
10	50	60	.50
25	10	30	1.00
25	30	30	0.93
25	50	30	.58

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[7] Willard and Young, THIS JOURNAL, 51, 149 (1929).

[8] Willard and Young, ibid., 50, 1322 (1928); see also Furman, ibid., 50, 755 (1928).

over a small flame for the time indicated, then cooled to 30–35°, and the excess of ceric sulfate titrated electrometrically with standard ferrous sulfate. The results are shown in Table I.

These results indicate that selenious acid is not oxidized by ceric sulfate in a hot solution of moderate acid concentration and only very slightly oxidized in a solution of low acidity.

Measured portions of a 0.9 N tellurite solution were diluted with water, acid and 25 cc. of 0.09611 N ceric sulfate to 200 cc., and treated in the same way as the solutions for the experiments in Table I. The results obtained are shown in Table II

Thus tellurous acid is only slightly oxidized under the conditions used in these experiments.

Since dichromate may be used, either in a hydrochloric or a sulfuric acid solution, to determine tellurous acid in the presence of selenious acid,[4,5,6] and since ceric sulfate may be used to oxidize chromic salt quantitatively to chromic acid in sulfuric acid solution,[9] it seemed obvious that

TABLE III

OXIDATION OF TELLUROUS ACID BY CERIC SULFATE USING CHROMIC SALT AS CATALYST

Expt	H_2SO_4 (sp gr 1 5) before ox, cc	Time at h p, min	Vol during ox, cc	0 08 *N* $Cr_2(SO_4)_3$ added, cc	0 09611 *N* $Ce(SO_4)_2$ added cc	0 1 *N* $Ce(SO_4)_2$ used, cc	Te taken, g.	Te found, g
1[a]	10	5	200	10	30	22 43	0 1434	0.1430
2	10	10	200	10	50	22 4i	1434	.1432
3	10	30	200	10	50	22 49	1434	.1434
4	10	10	200	5	50	22 47	1434	.1432
5	10	30	200	5	50	22.49	.1434	.1434
6"	10	30	200	2	50	21 82	.1434	.1391
7	30	10	200	5	50	22 47	.1434	.1432
8	50	10	200	5	50	22.51	.1434	.1435
9"	10	20	200	5	35	22.41	.1434	.1429
10	10	10	200	5	75	22.46	.1434	.1432
11	10	10	100	5	50	22.47	.1434	.1432
12	20	20	300	5	50	22 46	.1434	.1432
13	10	10	200	5	50	8.99	.0574	0573
14	30	10	200	5	50	9.00	0574	.0574
15	10	20	200	5	75	44 98	.2868	2867
16	20	20	200	10	100	67 49	.4302	4302
17[b]	10	10	200	5	50	22 50	1434	.1434
18[b]	30	10	200	5	50	22.55	.1434	.1437
19[a,b]	50	10	200	5	50	22.65	.1434	1444
20[c]	10	10	200	5	50	22 54	1434	1437
21"	10	10	200	5	50	22 52	1434	.1436
22"	10	10	200	5	50	22 55	.1434	.1437

[a] In these experiments the conditions were not correct for quantitative results
[b] 0.15 g. of Se added. [c] 0.30 g. of Se added [d] 0 15 g of Se + 0 30 g. of Cu added
[e] 0.30 g. of Se + 0 30 g. of Cu added.

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[9] Willard and Young, THIS JOURNAL, 51, 139 (1929).

chromic salt should catalyze the reaction between ceric sulfate and tellurous acid. Ceric sulfate oxidizes the small amount of chromic salt to chromic acid, which, after oxidizing tellurous acid, would be reoxidized by the ceric sulfate. To test this point, solutions were prepared as for the experiments in Table II, except that additions were made of chromic sulfate, and in some cases of selenious acid and copper sulfate, and the volume of the solution at the time of oxidation was varied. The treatment of the solutions was the same as for the experiments in Table II. Results are shown in Table III.

The above data show that the oxidation of tellurous acid by ceric sulfate in the presence of chromic salt as catalyst is quantitative over wide variations in acid concentration, excess of oxidizing agent and time of its action, volume of solution in which the oxidation is carried out, amount of chromic salt as catalyst and tellurous acid content. Selenious acid does not interfere if the sulfuric acid concentration at the time of oxidation is not too high. Cupric salts are without effect. The method offers a much wider possibility of variation in conditions than does the oxidation of tellurous acid by dichromate in hydrochloric acid solution, and is more rapid. The same is true in comparing it with the oxidation of tellurous acid by dichromate in sulfuric acid solution, though the experiments in Table III show that a much wider range of conditions could be developed for this latter method than those described by Schrenk and Browning.[6]

Also, preliminary experiments have shown the possibility of using chromic salt as catalyst in many oxidation reactions in which ceric sulfate alone is not effective, for example, in the oxidation of certain organic substances.

Summary

1. Selenious acid is not oxidized by ceric sulfate in hot sulfuric acid solution. Tellurous acid is oxidized only to a very slight extent under the same conditions.

2. A rapid quantitative method for tellurous acid has been developed, based upon its oxidation in hot sulfuric acid solution by ceric sulfate in the presence of chromic sulfate as catalyst. Selenious acid and cupric salts do not interfere.

3. Attention is called to the possibility of using chromic sulfate as catalyst in other oxidation reactions in which ceric sulfate alone is not effective, especially in the oxidation of certain organic substances.

ANN ARBOR, MICHIGAN

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

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. XIII. THE DETERMINATION OF MERCUROUS MERCURY

BY H. H. WILLARD AND PHILENA YOUNG

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Introduction

Few of the volumetric oxidation or reduction methods for mercurous mercury afford a separate estimation of it in the presence of mercuric ion. Among the procedures which accomplish this may be mentioned (1) its reduction by potassium iodide to mercury, followed by addition of excess standard iodine solution, and determination of the excess iodine with thiosulfate;[1] (2) its precipitation as mercurous oxalate by excess standard oxalate, the excess oxalate in the filtrate being determined with permanganate;[2] **(3)** its oxidation with excess standard permanganate, followed by addition of excess standard ferrous sulfate and back titration with permanganate;[3] (4) its precipitation by excess standard sodium chloride solution, followed by filtration, precipitation of the mercuric salt with hydrogen sulfide, filtration, removal of hydrogen sulfide by boiling and titration of the excess sodium chloride with standard mercurous nitrate, using diphenylcarbazide as indicator[4]—obviously a tedious process; (5) its titration in strong hydrochloric acid solution with potassium iodate, using chloroform as indicator.[5] This last method appears to be the one most widely used.

The present paper is a study of the oxidizing action of ceric sulfate on mercurous ion and describes a volumetric procedure for mercurous mercury, applicable in the presence of large amounts of mercuric salts.

Experimental

Mercurous sulfate was made by adding slowly a solution of mercurous perchlorate to dilute sulfuric acid. The precipitate was thoroughly washed, then suspended in 0.1 *M* sulfuric acid. This mixture, after being stirred for five to six hours, was filtered. The mercurous sulfate solution thus obtained was standardized gravimetrically by precipitating the mercurous mercury as chloride and drying the precipitate to constant weight over phosphorus pentoxide. The results of three experiments gave 0.0295, 0.0295 and 0.0296 g. of mercury per 100 cc. The filtrate from the mercurous chloride gave no test for mercury when made ammoniacal and treated with hydrogen sulfide and solid ammonium chloride.

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[1] Hempel, *Ann.*, 110, 176 (1859).

[2] Peters, *Z.* anorg. Chem., 24, 402 (1900).

[3] Randall, Am. J. Sci., [4] 23, 137 (1907).

[4] Oddo, *Gazz. chim.* ital., 39, I, 666 (1909).

[5] Jamieson, *Am.* J. *Sci.*, 33, 349 (1912).

The ceric sulfate solution was part of a large supply made by the method described by the authors[6] from high grade ceric oxide and was 0.5 *M* in sulfuric acid. It was standardized against sodium oxalate.[7] The ferrous sulfate solution was standardized electrometrically against standard ceric sulfate.[7]

Measured portions of the standard mercurous sulfate were taken, diluted with water, sulfuric acid (sp. gr. 1.5) and 0.09611 N ceric sulfate to a definite volume, heated to boiling and held just below the boiling point over a small flame for the time indicated. The solutions were then cooled to 30–35° and titrated electrometrically with standard ferrous sulfate. The results of a number of experiments are indicated in Table I.

TABLE I

THE OXIDATION OF MERCUROUS MERCURY WITH CERIC SULFATE IN ACID SOLUTION

Expt.	H_2SO_4, (sp. gr. 1.5) before ox., *cc.*	Time at b.p., min.	Vol. during ox., *cc.*	0.09611*N* $Ce(SO_4)_2$ *added, cc.*	0.1 N $Ce(SO_4)_2$ used, *cc.*	Hg_2^{++} taken, g.	Hg_2^{++} found, g.
1	10	15	200	25	1.47	0.0295	0.0295
2	10	30	200	25	1.48	.0295	.0297
3	30	15	200	25	?	.0295	?
4	50	30	200	25	1.48	.0295	.0297
5	10	30	300	25	1.48	.0295	.0297
6	50	30	300	25	1 47	.0295	.0295
7	10	30	200	15	?	.0295	?
8	10	60	200	15	1.46	.0295	.0293
9	50	60	200	15	?	.0295	?
10	10	15	200	50	1.48	.0295	.0297
11	50	15	200	50	?	.0295	?
12[a]	10	30	200	25	1.47	.0295	.0295
13[b]	10	30	200	25	1.50	.0295	.0301
14	10	15	200	25	0.73	.0148	.0147
15[c]	50	15	200	25	0.75	.0148	.0150
16"	10	30	200	25	2.20	.0443	.0442
17	10	30	200	50	2.20	.0443	.0442
18	15	30	300	50	2.94	.0590	.0590
19	20	30	400	50	?	.0885	?
20	20	60	400	50	4.42	.0885	.0887
21[d]	10	30	200	50	1.49	.0295	.0297
22[d]	20	60	400	50	4.43	.0885	.0889

[a] 5 cc. of $HClO_4$ (70%) present. [b] 5 cc. of HNO_3 (sp. gr. 1.42) present.
[c] End-point poor. [d] 0.3 g. of Hg^{++} present.

In Expts. 17, 18, 20, 21 and 22 blank corrections of 0.07, 0.10, 0.17, 0.15 and 0.21 cc., respectively, have been applied to the volume of 0.1 N ceric sulfate used for the oxidation. If more than 30–35 mg. of mercurous mercury is present in a sample, it is always necessary to run a blank determination, using the same quantities of reagents and the same procedure

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[6] Willard and Young, THIS JOURNAL, 51, 149 (1929).

[7] Willard and Young, *ibid.*, 50, 1322 (1928); see also Furman, *ibid.*, 50, 755 (1928).

as for the unknown. An amount of mercuric sulfate, free from mercurous ion, approximately equal to that in the unknown should be added to the blank before heating. Mercuric ion in considerable amount tends to cause a slight decomposition of ceric sulfate in hot solution.

The experiments in Table I show that mercurous ion is quantitatively oxidized to mercuric ion provided that a large excess of ceric salt is used, that the acidity of the solution is not too great and that the oxidizing agent is allowed to act in hot solution for thirty to sixty minutes. A moderate amount of perchloric acid causes no interference but nitric acid produces a slight effect. A large amount of mercuric ion does not interfere if a blank correction is made for its slight action on ceric sulfate in hot solution.

Summary

An accurate method has been developed for mercurous mercury, based upon its oxidation in hot sulfuric acid solution by excess ceric sulfate and titration of the excess electrometrically with standard ferrous sulfate. Mercuric ion in large amount does not interfere.

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[Contribution from the Kent Chemical Laboratory of the University of Chicago]

PHOTOCHEMICAL STUDIES. XI. THE QUANTUM EFFICIENCY OF OZONE FORMATION IN THE FLUORITE REGION

By William E. Vaughan and W. Albert Noyes, Jr.

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The photochemistry of the range of wave lengths below those transmitted by quartz has received scant attention. The difficulty of obtaining monochromatic radiation of sufficient intensity to produce measurable chemical effects in this region of the spectrum is great. In a recent article the photochemical decomposition of ammonia was studied in the fluorite region.[1] By a comparison of the rate of ozone formation with the rate of decomposition of ammonia under the influence of those wave lengths transmitted by fluorite but not by quartz, it was possible to calculate the quantum efficiency of the latter reaction by making the following assumptions: (I) that the photochemical decomposition of ammonia is represented by the equation $2NH_3 = N_2 + 3H_2$; (2) that the absorption of ammonia is identical with that of oxygen in this range of wave lengths; **(3)** that two molecules of ozone are formed per quantum of radiation absorbed by oxygen. With these assumptions it was possible to show that the average quantum efficiency of ammonia decomposition is about 0.7 for the approximate spectral region 150mμ to 190mμ.

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[1] Kassel and Noyes, This Journal, 49, 2495 (1927).

Since the publication of this work, additional confirmation has been received for the validity of the second assumption.[2] The validity of the first assumption is not so certain,[3] since some of the decomposition products may not appear in the gas phase. The possible formation of hydrazine as an intermediate product hardly offers a satisfactory explanation of the discrepancy.[1,4] The quantum efficiency would, therefore, be slightly higher than 0.7.

The present research was undertaken with the object of investigating the validity of the third assumption, namely, that two molecules of ozone are formed from oxygen per quantum absorbed. The work has been carried out at atmospheric pressure. Since oxygen has a region of continuous absorption below 175mμ,[5] this reaction is a convenient one for measuring light intensities in the range of wave lengths transmitted by fluorite but not by quartz. This investigation, it is hoped, will establish the quantum efficiency of this reaction so that it may be used in the future.

I. Experimental Procedure

The first requisite for the determination of the quantum efficiency of ozone formation is an accurate method of analysis. After a review of the literature and an investigation of the various methods for the quantitative determination of small amounts of ozone,[6] it was decided that the most reliable method was by absorption of the ozone in a solution of potassium iodide. The solutions were acidified and to each one was added a definite quantity of starch freshly prepared each few days. All of the calculations are based on the equation

$$2H^+ + O_3 + 2I^- = O_2 + I_2 + H_2O \qquad (1)$$

Some uncertainty exists as to the exactness of this equation, but it undoubtedly represents the main course of the reaction. In basic solution there may be some simultaneous reaction of the type $I^- + O_3 = IO_3^-$.

The source of radiation was a condensed discharge through hydrogen at a pressure of about 0.1 mm. Current was supplied from the secondary of a 1-kw. transformer with a peak voltage of 30,000. The dimensions of the discharge tube are given in Fig. 1. The electrodes (A) were made of iron. The windows (B) and (C) were of fluorite. The ends of the discharge tube were carefully ground, so that there was little contact between the hydrogen and the picein wax used. A continuous flow of hydrogen was maintained through the discharge tube. Hydrogen was prepared in an ordinary electrolytic gen-

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[2] Bonhoeffer and Farkas, *Z. physik. Chem.*, 134,337 (1928).

[3] Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, 12, 692 (1926); Mitchell and Dickinson, THIS JOURNAL, 49, 1478 (1927); Taylor and Bates, *Proc. Nat. Acad. Sci.*, 12, 714 (1926); Bates and Taylor, THIS JOURNAL, 49,2438 (1927).

[4] Elgin and Taylor, *ibid.*, 51,2059 (1929).

[5] See "Molecular Spectra in Gases," by Kemble, Birge, Colby, Loomis and Page, *Bull. Nat. Research Council,* 11, Part 3, 244 (1926).

[6] Allen, M. S. "Dissertation," University of Chicago, 1929; *Ind. Eng. Chem., Analytical Edition,* 2, 55 (1930).

erator and passed continuously over heated platinized asbestos, sodium hydroxide sticks and phosphorus pentoxide before being admitted to the discharge tube through the capillary (I)). (F) was attached to a mercury diffusion pump backed by an oil pump. The pressure of hydrogen in the tube remained quite constant.

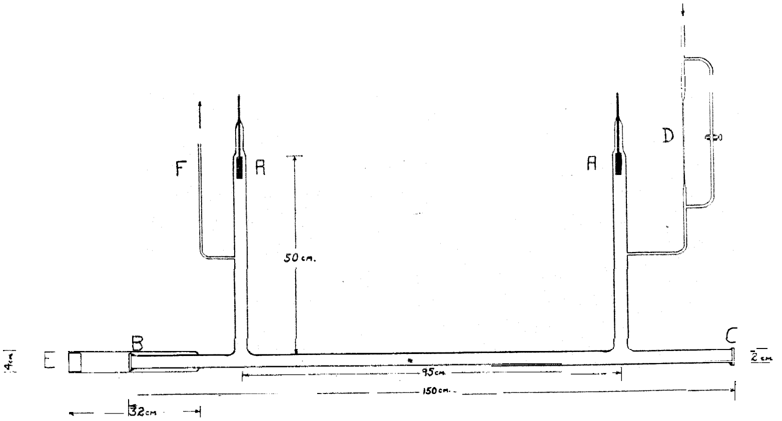

Fig. 1.

The radiation given out by the discharge tube formed a slightly diverging beam. The intensities were measured by means of two different thermopiles, both calibrated by a radiation standard furnished by the Bureau of Standards.

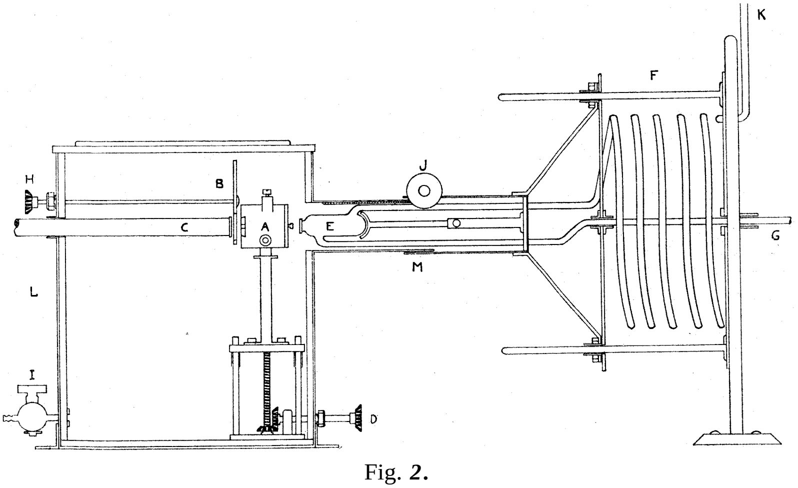

Fig. 2.

One end of the discharge tube (C) projected into the box shown in Fig. 2. This box was constructed of brass and no oil was used on any of the bearings. The box was not, of course, vacuum tight, but it was kept under slight positive pressure of gas transparent to the region of the spectrum under consideration. At first helium was tried, but it was found impossible to purify commercial helium satisfactorily at the rate of flow necessary. Consequently, attempts were made to use hydrogen and nitrogen. After many measurements of absorption in the fluorite region it was found that it was easier to obtain nitrogen of reproducible purity and this gas was used to fill the box in all of the final measurements.

The nitrogen was obtained from a cylinder. It was water-pumped and of 99.7% purity. It was passed first over heated copper turnings, then partially dried by sodium hydroxide sticks and finally passed through a charcoal trap immersed either in liquid air or in carbon dioxide snow and ether. The distance traversed by the radiation through the nitrogen was about 1.4 cm.

The thermopile (A) was fitted with a fluorite window and was arranged so that it could be lowered and raised by turning the handle (D). The reaction vessel (E) was 7.4 cm. in length and 2 cm. in internal diameter. It was arranged so that when the thermopile was lowered it could be moved forward to such a point that the window was the same distance from the discharge tube as the elements of the thermopile. The glass spiral (F) was of such length and flexibility that the reaction vessel could be moved without introducing any rubber tubing into the apparatus. The shutter (B) had three openings. On one was placed a piece of crystal quartz 3 mm. in thickness with the optical axis such that there was no polarization of the radiation traversing it. On the second opening was cemented a piece of optically plane pyrex 3 mm. in thickness. The third opening was left vacant.

The oxygen was streamed through the reaction vessel at various rates. It had already been shown[1] that the amount of ozone formed was independent over quite wide limits of the amount of oxygen passing through the reaction vessel in unit time. This is in agreement with tests made during the present experiments.

The oxygen was passed first over heated platinized asbestos, partially dried by passing over sodium hydroxide sticks and finally passed through a trap immersed in carbon dioxide snow and ether. It entered the reaction vessel through the spiral (F). The tube (G) was attached to two Fischer wash bottles containing either 0.01 or 0.001 M potassium iodide and 0.0013 M sodium hydroxide.

The first runs (shown in Table I) were made in the following manner: the thermopile (A) was raised to the position shown in Fig. 2 and the intensity of the radiation measured. The discharge tube had been allowed to run until the current through the transformer became constant. The intensity of the radiation transmitted by 1.4 cm. of nitrogen without filter through quartz and through pyrex was determined before each run. The thermopile was then lowered and the reaction vessel (E) moved forward. The oxygen was allowed to pass through the reaction vessel for a definite length of time, the rate of flow being determined by a flowmeter (not shown). Following the run the intensity of the radiation was determined. Good agreement between the initial and final intensity readings was found in nearly every case. The rate of flow of oxygen was varied by a factor of about forty without causing a definite trend in the amount of ozone found.

A definite fraction (50 cc. out of 152 cc.) of the potassium iodide solution from the first wash bottle was acidified with 6 cc. of 0.05 M sulfuric acid and 2 cc. of a clear starch solution was added. The mixture was well shaken and allowed to stand for about ten hours. A sample from the second wash bottle was treated in exactly the same manner. In a few cases a third wash bottle was also used. In no case did the solution in the third wash bottle give any test for iodine liberated and usually the amount in the second wash bottle was small.

The intensity of coloration was compared in Nessler tubes with standards made in exactly the same manner except that a carefully measured (by pipet) amount of 2.48×10^{-5} M solution of iodine dissolved in potassium iodide was added. These standards were allowed to stand for the same length of time as the unknown.

The fraction of the total radiation absorbed by the oxygen was determined in two different manners In one the other end of the discharge tube (B) (Fig 1) was used. The tube at (E) was attached to an iron cylinder by wax. A thermopile was placed in the iron cylinder The cylinder was evacuated to a pressure of about 10^{-5} mm. by mercury diffusion pumps. Mercury vapor was excluded by a trap immersed in liquid air. The absorptions of nitrogen and of oxygen were determined for a 19-cm. path In this manner it was found that **3.3%** of the radiation was absorbed by oxygen that was not absorbed by nitrogen. The absolute measurement of the amount of radiation seemed to have little significance.

The second method was to replace the reaction vessel by a tube of exactly the same length fitted with fluorite windows at both ends. A thermopile without fluorite windows was placed directly in back of the absorption tube. The tube was evacuated and the deflection measured. The deflection was measured again when thr tube was filled with oxygen. When the fluorite window used on the reaction vessel was interposed, three determinations gave 3.0, 3.5 and 3.1 as the percentage decrease in the deflection when the tube was filled with oxygen.

The calculation of the fraction of the incident radiation absorbed can only be made by an indirect method. Let us consider a perfectly parallel beam of radiation. Then we may make the following comparisons, where I represents intensity.

Through oxygen

I_1 Fluorite window I_2 oxygen I_3 Fluorite window I_4

With cell evacuated

I_1 Fluorite window I_2 vacuum I_2 Fluorite window I_5

The fraction $(I_5 - I_4)/I_5$ is measured directly in the experiments. Put $I_1/I_2 = a$, $I_3/I_4 = b$ and $I_2/I_5 = c$. The fraction of the incident radiation absorbed by the oxygen is $(I_2 - I_3)/I_1 = X$. Put $(I_5 - I_4)/I_5 = Y$. We now find that

$$X = [c-(1-Y)b]/ac \qquad (2)$$

The measurement of the quantities a, b and c was accomplished by removing the windows from the absorption cell and determining the absorption of the fluorite when the radiation had traversed nitrogen and the proper length of column of oxygen. In this way it was found that $a = 1.160$, $b = 1.134$ and $c = 1.137$, each value being the average of a large number of readings. Hence

$$X = (1.137 - 0.968 \cdot 1.134)/1.160 \cdot 1.137 = 0.030$$

Table I gives a summary of the data obtained in preliminary runs made by the method described above.

Another series of measurements was made in which the cell used previously to determine the absorption was used as a reaction vessel. Since this cell could not be moved, the light intensity back of the cell (through oxygen) was measured during the run. The procedure for the determination of ozone was the same as that used previously, except that in half of the runs an acid solution of potassium iodide was used in place of a basic solution.

TABLE I

PRELIMINARY DETERMINATION OF QUANTUM EFFICIENCY

Iodine solution, 0.0000248 M. Thermopile, 14.3 ergs/mm.^{2}/sec./cm. Area of window, 154 mm.^{2} Wave length (av.), 175mμ. Fraction absorbed, 0.03

Run	Total cc. of I_2	Length of run, hrs.	Av. defl., cm.	Molecules of O_3	No. of quanta	M/N
1	9.4	3	1.09	1.41×10^{17}	$6\ 92 \times 10^{16}$	2.0
2	9 9	3	1.08	1.49×10^{17}	6.85×10^{16}	2.2
3	13 6	4	1.13	2.04×10^{17}	9.57×10^{16}	2.1
4	12.2	3	1.19	1.83×10^{17}	7.56×10^{16}	2.4
5	8 5	3	11.96	1.28×10^{17}	$6\ 03 \times 10^{16}$	2.1
						Av. 2 2

Since a different fluorite window was used at the front of the reaction vessel in these experiments, it was necessary to redetermine the absorption. Table II gives the data obtained in making these determinations.

TABLE II

ABSORPTION OF OXYGEN

Defl. av. vacuum, cm.	No. of readings	Defl. av. oxygen, cm.	No. of readings	Fraction $(I_5 - I_4)/I_5$ av.
1.70 (0)	14	1.62 (2)	12	
1.70 (1)	12	1.61 (5)	10	
1.69 (3)	14	1.63 (1)	11	
1.70 (0)	10	1.60 (3)	11	
1.69 (6)	10	1.61 (4)	10	0.048 ± 0.006

By the use of Equation 2 it is found that the fraction of the incident radiation absorbed by the oxygen is 0.044.

Since the radiation intensity is measured back of the cell through oxygen, it is necessary to find the factor by which it must be multiplied to obtain the incident intensity. Since the beam was not perfectly parallel, but diverged somewhat, this factor could not be calculated directly. However, this factor was obtained by removing the reaction vessel and obtaining the ratio of the deflection at 1.4 cm. from the discharge tube to the deflection at 8.8 cm. Eight determinations gave 4.9 as the average ratio. The observed intensity must be multiplied, therefore, by $4.9 \cdot 1.137 \cdot 1.134/$-0.952 or 6.64. Direct measurement of this factor gave 6.6.

Table III gives the data obtained in this manner. Absorption of the ozone was carried out in acid (with hydrochloric acid) solution of potassium iodide in the last three runs. It has been shown previously[7] that ozone has an apparently higher oxidizing power in acid solution than in neutral or basic solution. This fact was studied[6] and it was found that within the experimental error 1.25 times as much iodine was liberated when ozone was absorbed in acid solution as when it was absorbed in neutral or basic

[7] Mellor, "Comprehensive Treatise," Longmans, Green and Co., London, 1922. Vol. I, p. 905.

solution and then acidified. The number of molecules of ozone obtained by direct calculation in the last three runs in Table III is multiplied by 0.8.

TABLE III

QUANTUM EFFICIENCY OF OZONE FORMATION

Iodine solution, 0.00005 *M*. Thermopile, 2 8 ergs/mm.^{2}/sec./cm. Area of window, 73 mm.^{2} Wave length (av.), 175mμ. Fraction absorbed, 6 64·0.044

Run	Total cc of I_2	Length of run, min.	Av defl, cm	Molecules of O_3	No. of quanta	*M/N*
6	18 0	395	2 28	5 45 × 10^{17}	2 88 × 10^{17}	1 9
7	8 8	272	2 39	2 64 × 10^{17}	2 07 × 10^{17}	1 3
8	18 2	385	2 41	5 52 × 10^{17}	2 96 × 10^{17}	1.9
9	22 8	355	2 46	5 53 × 10^{17}	2 78 × 10^{17}	2 0
10	19 8	325	2 48	4 80 × 10^{17}	3 57 × 10^{17}	1 9
11	198	300	2.38	4.80 × 10^{17}	2.28 × 10^{17}	2.1
						Av. 1 85
					(Omitting second)	**Av.** 2 0

It is difficult to form a very precise idea of the probable accuracy of the values obtained for the quantum efficiency. The determination of the number of molecules of iodine liberated is undoubtedly the main cause for variation among the various results. On the average these values should be good to better than 10%. The error in the calibration of the thermopile is undoubtedly small compared to other errors. The determination of Y in Equation 2 is somewhat uncertain, but the values used should be accurate to somewhat better than 10%. The quantities *a*, b and *c* in Equation 2 are of importance; a and *c* are each known with a probable error not exceeding 1%, but small errors in *c* and b would produce a relatively large error in X. These values were carefully determined and when all the factors entering into Equation 2 are considered, it is probable that the value of X is accurate to within 15%.

It seems safe to state that the quantum efficiency of ozone formation for radiation transmitted by fluorite is 2.0 ± 0.3.

It should be pointed out that the error in choice of the average wave length of the active radiation is certainly small compared to other errors. It is recognized that the quantum efficiency is not obtained for monochromatic radiation. A discussion of the possible effect of change of wave length will be given in the next section. However, since no lenses were used errors due to such factors as chromatic abberration are negligible.

Using a different type of discharge, Kassel and Noyes[1] showed that approximately **3.5** times as much ozone is formed when fluorite windows are used as with quartz. One attempt was made in these experiments to determine the amount of ozune formed by radiation transmitted by quartz, but the inaccuracies in the determination of the ozone and in the measurement of the light absorption were so great that the matter was not pursued further. Since absorption would not be complete (about

15%[8] for the shortest wave length transmitted by quartz) whereas no greatly increased absorption was observed for a 19-cm. path, it seems probable that a very large fraction of the radiation absorbed in these experiments lies below the limit of transmission of quartz. Except for certain isolated bands, nitrogen is quite transparent to the region of the spectrum under consideration. There are several bands near 170mμ and stronger bands at 145mμ.[9] The limit of transmission of the nitrogen is probably determined by the impurities it contains. The fluorite used transmitted to about 140mμ. The probable limits of the spectrum involved in the above experiments are from about 190mμ to somewhat less than 170mμ.

II. Theoretical Discussion

It has been shown that the oxygen molecule is normally in a $^3\Sigma$ level and that this is the ground level for both the atmospheric absorption bands and the Schumann–Runge bands.[10] The interpretation of the atmospheric absorption bands is now quite satisfactory[11] and is found to involve a $^3\Sigma - {}^1\Sigma$ transition. The $^1\Sigma$ level lies only 1.62 volts above the normal level and combines with it exceedingly weakly. To all intents and purposes oxygen at ordinary pressures and thicknesses is practically completely transparent to radiation of wave lengths found in the atmospheric absorption bands.

The Schumann bands are found to involve in all probability a $^3\Sigma - {}^3\Sigma$ transition.[12] They involve, in absorption, a transition from the normal to a 6.09-volt electronic level. The convergence limit of this series of bands occurs at 175.1mμ, or a little over 7 volts. Dissociation of the molecule should, therefore, be brought about by radiation of wave length shorter than this value. The products of dissociation should be one normal and one excited atom. The exact state in which this excited atom will leave the molecule is uncertain[13] but it may lie between 1.5 and 2.0 volts above the normal level.[14] Due to the fact that no exact determination of the heat of dissociation of oxygen by calorimetric methods has been made, this level cannot be calculated indirectly.

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[8] See "International Critical Tables," McGraw-Hill Book Co., New York, 1929, Vol. V, p. 269.

[9] Hopfield, *Phys. Rev.*, 31, 1131 (1928).

[10] Ossenbruggen, *Z. Physik*, 49, 167 (1928).

[11] Mulliken, *Phys. Rev.*, 32, 880 (1928); Giauque and Johnston, THIS JOURNAL, 51, 1436, 3528 (1929).

[12] See Mulliken, *Phys. Rev.*, 32, 213 (1928).

[13] The earlier idea that the atom was in an energy level differing by only a few hundredths of a volt from that of the normal atom has since been shown to be very doubtful. *Cf.* "Molecular Spectra in Gases," Kemble, Birge, Colby, Loomis and Page, *Bull. Nat. Res. Council*, Vol XI, Part 3, No. 57 (1926).

[14] See Kaplan, *Phys. Rev.*, 31, 1126 (1928); Herzberg, *Z. physik Chem*, 4B, 228 (1929).

In the range of wave lengths longer than the convergence limit, excited molecules in a $^3\Sigma$ state are produced by absorption of radiation. Ozone is, however, produced in this region of the spectrum. Warburg[15] has studied the quantum efficiency of ozone formation at relatively high pressures at 207mμ and 253mμ and finds values of about 2 at about 47 atmospheres, becoming lower at higher pressures. The quantum efficiency is lower at the longer wave length.

In view of the present knowledge of band spectra the primary process in the region of the Schumann bands at wave length greater than 175mμ is the production of an excited molecule and this may be followed by some such reaction as

$$O_2' + O_2 = O_3 + O \quad (3)$$

A second molecule could be produced by the reaction

$$O_2 + O = O_3 \quad (4)$$

However, this latter reaction, in accord with well recognized principles, can only take place as the result of triple collisions or on the walls, since otherwise the molecule would still possess energy adequate to produce redissociation. Similarly, the reaction

$$O + O = O_2 \quad (5)$$

could only take place in this fashion. Enough is not known to permit an adequate calculation of the relative probabilities of Reactions 4 and 5, but unless the light intensity were exceedingly great the chance of Reaction 5 would be small. Also, the formation of ozone by Reaction 4 would be less exothermic than Reaction 5, so that the probability of its occurrence would be greater. Hence it would not be surprising if two molecules of ozone were produced by wave lengths longer than the convergence limit.

In the region of continuous absorption below the convergence limit, two oxygen atoms, one of which is excited, are produced. There are now several possibilities. The normal atom may undergo Reaction 4 by triple collision. The excited atom may lose its energy by radiation and subsequently undergo Reaction 4. In this event the quantum efficiency would be two in this region of the spectrum. If the energy of the excited atom is sufficiently large, it might lose its energy to an oxygen molecule by a collision of the second kind, thereby raising the latter to some higher vibration state of either the normal or the 1.62 electron level. In either event the excited molecule produced could not undergo Reaction **3.** As a result of a triple collision with molecules in higher vibration states it might undergo the reaction

$$O_2'' + 2O_2 = 2O_3 \quad (6)$$

Since the production of two molecules of ozone from three molecules of oxygen involves the absorption of energy corresponding to about 2.5 volts,

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[15] Warburg, *Z.* Elektrochem., **27,** 133 (1921). See Wulf, THIS JOURNAL, 50, 2596 (1928), for a discussion of the possible relationship of this work to the existence of O_4.

the two oxygen molecules in the normal state must possess an energy of 2.5 − E_1 volts, where E_1 represents the energy of the molecule O_2'' above the normal. Since E_1 is not known, it is impossible to make any definite statement in this connection. Reaction 6 must not be considered as impossible, however.

Still one other possibility may be mentioned. Since Reaction 4 is exothermic and can occur only as the result of triple collisions, the third molecule involved may be raised to a higher vibration or electronic level. However, since the energy available by Reaction 4 only slightly exceeds 1 volt, this possibility would seem to be of small importance.

As a result of these considerations we see that the quantum efficiency of ozone formation to be expected from theoretical consideration agrees with experiment well within the experimental error. A value slightly greater than two would not be impossible.

Eucken[16] has studied the formation of ozone by short wave length radiation and finds a negative temperature coefficient. This effect is particularly noticeable at low oxygen pressures. Eucken attempts to explain this phenomenon by assuming that the mean life of activated molecules in high rotation states is shorter than when the rotational quantum number is less. Another effect may also be of importance. The oxygen atoms produced by Reaction 3 may have time to diffuse to the walls and be removed before undergoing the triple collision necessary for Reaction 4. This effect would be particularly noticeable at low pressures. Since third order reactions have, in general, negative temperature coefficients, the necessary triple collisions might occur more often at low temperatures. In the region of continuous absorption the temperature coefficient should be unity unless the effect of the walls in removing the oxygen atoms is of importance. Since this removal process may be more important at low than at high temperatures, this effect cannot be neglected.

Summary

1. Approximately two molecules of ozone are formed per quantum absorbed by oxygen in the fluorite region.

2. A short theoretical discussion is given. The value found is in agreement with theory, although a slightly higher value would not he impossible.

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[16] Eucken, *Z. physik. Chem.*, 107, 436 (1923).

[CONTRIBUTION PROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OP MICHIGAN]

DETERMINATION OF MERCURY AS METAL BY REDUCTION WITH HYDRAZINE OR STANNOUS CHLORIDE

BY H. H. WILLARD AND A. W. BOLDYREFF

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Introduction

The principal errors in determining moderate and large amounts of mercury gravimetrically by reduction to metal are caused by: (1) loss through volatility during the process of reduction, if it is carried out at an elevated temperature; (2) loss in the process of filtration—fine particles going through the filter; (3) loss through volatility in the process of drying. The loss of mercury from hot solutions of its salts, from suspensions of fine particles of mercury, and from metallic mercury on drying has been sufficiently emphasized by Howard[1] as early as 1904. Therefore, the reaction and the conditions for reduction, filtration and drying must be so chosen that the whole process can be carried out at room temperature, that the precipitated mercury is not in too fine a state of division and that the time of drying is as short as possible.

The following reducing agents were tested: sodium arsenite, phosphorous acid, hypophosphorous acid, hydrogen peroxide, stannous chloride, hydroxylamine and hydrazine. Hydrazine hydrate in an ammoniacal solution and stannous chloride in a hydrochloric acid solution were found most satisfactory.

Hydrazine Reduction.—Jannasch[2] has shown that mercury can be separated from such metals as copper, bismuth, lead, cadmium, arsenic, antimony, zinc and metals of the iron group by reduction with hydrazine in an ammoniacal or a weakly acid solution. However, on account of the danger of loss he weighed the mercury as sulfide.

The separation of mercury from other metals by reduction with hydrazine has also been studied by Knoevenagel and Ebler.[3]

In their work on the atomic weight of mercury, Easley and Brann[4] and later Honigschmid, Birckenbach and Steinheil[5] removed mercury from the solutions of its halides by reduction with hydrazine. The former found that some of the precipitated mercury was always in such a fine state of division that it passed through the densest filters.

Duccini[6] applied the reaction to the quantitative determination of mer-

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[1] Howard, *J. Soc. Chem. Ind.*, 23, 151 (1904).

[2] Jannasch, *Ber.*, 31, 2377 (1898); "Prakt. Leitfaden d. Gewichtsanalyse," Veit and Co., Leipzig, 1904.

[3] Knoevenagel and Ebler, *Ber.*, 35, 3055 (1902).

[4] Easley and Brann, THIS JOURNAL, 34, 137 (1912).

[5] Hönigschmid, Birckenbach and Steinheil, *Ber.*, 56, 1212 (1923).

[6] Duccini, *Gazz. chim. ital.*, 43, 693 (1913).

cury, weighing it as metal. Briefly, his procedure consisted in precipitating mercury from a potassium hydroxide solution with an excess of hydrazine sulfate, filtering through a small paper filter after six to eight hours' standing, washing first with dilute hydrochloric acid, then with water, alcohol and ether, drying for five to six hours in a desiccator over calcium chloride and weighing. Under these conditions the finely divided mercury settles very slowly, and this method of drying can hardly be recommended.

In this work the question of drying precipitated mercury was first studied. Dick[7] recommends washing precipitates with alcohol and ether, followed by drying in a vacuum desiccator. This procedure was not considered advisable, because it requires two wash solutions, the use of a vacuum desiccator, and because even pure ether usually contains enough peroxide to tarnish the surface of mercury. It is strange that the use of acetone in preference to alcohol and ether has not found a wider application for drying precipitates. Barnebey[8] in a note on the use of acetone for drying chemical utensils, recommended it in place of alcohol and ether. Easley[9] showed that a single globule of mercury could be dried without loss by washing with acetone and warming up to 30–35° for half an hour.

Experimental

In this work the method of drying was as follows: the crucibles and precipitates were washed five times with redistilled acetone and air-dried at room temperature on the suction flask by sucking through them for five minutes air previously dried by calcium chloride (see Fig. 1).

The reproducibility of the weights is shown in Table I. A slight difference between the "acetone-dried weight" and the "oven-dried weight" is undoubtedly due to a trace of acetone being adsorbed by the pores of

TABLE I

DRYING OF CRUCIBLES

Crucible	First acetone drying	Second acetone drying	Oven drying at 120°
1	17.1666	17.1665	
2	15.5768	15.5768	
3	16.1287	16.1286	
4	16.0821	16.0821	
5	13.8332	13.8333	13.8329
6	17.0914	17.0914	17.0912
7	16.3581	16.3580	16.3581
8	17.9009	17.9010	17.9006
9	13.2854	13.2854	13 2852
10	16.3556	16.3556	16.3554

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[7] Dick, *Z anul. Chem* , **77,** 352 (1929)

[8] Barnebey, THIS JOURNAL, **37,** 1835 (1915)

[9] Easley, *ibid.*, **31,** 1207 (1909).

the crucible. Whenever the chemical nature of the precipitate permits the use of acetone, and especially when heating must be avoided, the use of this simple and rapid method is recommended.

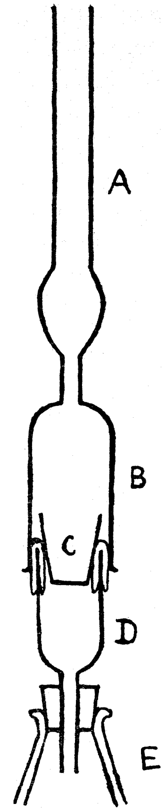

Fig. 1.—Apparatus used in drying crucibles. A, calcium chloride tube; B, glass adapter sealed to the calcium chloride tube and fitting tightly over the rubber Gooch tubing of the crucible holder; C, crucible; D, crucible holder; E, suction flask.

Attention was next turned to the process of filtration. The precipitation was always carried out in the cold. Filtered concentrated ammonium hydroxide was first added, and then roughly twice the theoretical amount of hydrazine hydrate. The rate of precipitation was found to increase with the hydroxyl-ion concentration. The speed of settling and the coarseness of the particles of precipitated mercury increased at first, but decreased with further increase in concentration of ammonium hydroxide, due, undoubtedly, to adsorption of hydroxyl ions on the surface of the particles of mercury, preventing them from coalescing.

For optimum conditions, 10 cc. of freshly filtered ammonium hydroxide (sp, gr. 0.90) should be added to every 50 cc. of the neutral solution. The precipitation is most conveniently carried out in a tall narrow beaker. It is preferable to keep the volume of the solution as small as possible (50 to 100 cc.).

Under these conditions the precipitate settles completely in one to two hours, but may stand longer if preferred. The heavy gray powder can be filtered as it is or changed into droplets (to facilitate transfer and filtration) by adding to the solution 35 cc. of concentrated hydrochloric acid, stirring for a minute and making ammoniacal again. When time is an important factor, the precipitation is carried out in a centrifuge cup, the solution stirred for a minute to ensure complete reduction, and centrifuged for five minutes. All the mercury then collects into one or two large globules, except a few milligrams, which always remain in the form of a fine gray powder.

The precipitate is conveniently filtered through a porcelain filtering crucible, type A1,[10] previously dried with redistilled acetone and dry air, as already described. A Gooch crucible with asbestos or with precipitated gold mat and a Munroe crucible were used with equal success, but the porcelain filtering crucibles were finally used exclusively, because their weight is most reproducible.

After filtering, the precipitate is thoroughly washed with cold water.

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[10] Manufactured by the Staatliche Porzellanmanufaktur, Berlin.

The mercury in the crucible can be caused to collect into one drop by gently shaking the crucible, thus simplifying the washing; a few milligrams of mercury will, however, always remain in the form of a fine gray powder sticking to the pores of the crucible. The water is then washed out with pure redistilled acetone and the crucible air-dried for five minutes, as described above. After standing in the balance case for two minutes the crucible can be weighed.

The analyses of pure mercuric chloride solutions (prepared from 99.98% pure $HgCl_2$) and of nitrate solutions (prepared by dissolving specially redistilled mercury in nitric acid) are given in Table II.

TABLE II

DETERMINATION OF MERCURY BY REDUCTION WITH HYDRAZINE HYDRATE IN AN AMMONIACAL SOLUTION

	Mercury, g			
No.	Taken	Found	Corrected	Error, mg.
		Chloride Solutions		
1	1.8821	1.8801	1.8814	−0.7
2	1.3662	1.3652	1.3665	+ .3
3	1.2416	1.2405	1.2418	+ .2
4	1.0175	1.0168	1.0181	+ .6
5	0.5112	0.5096	0.5109	− .3
6	.1827	.1811	.1824	− .3
7	.1751	.1739	.1752	+ .1
8	.1533	.1519	.1532	− .1
9	.1132	.1120	.1133	+ .1
10	.0700	.0686	.0699	− .1
		Nitrate Solutions		
1	2.2247	2.2232	2.2245	− .2
2	1.8285	1.8282	1.8295	+1.0
3	1.5168	1.5146	1.5159	−0.9
4	0.8045	0.8033	0.8046	+ .1

From this table it is evident that the amount of mercury found is always less than the theoretical by a practically constant amount. That this loss was due only to volatility was proved by testing in each case the original beaker, the filtrate and the washings with ammoniacal sulfide, after first adding concentrated nitric acid to dissolve the mercury. In every case the transfer of the precipitate from the beaker to the crucible was found to be complete, and no mercury could be detected either in the filtrate or washings. Furthermore, in several experiments the air with which the mercury was dried was passed through a gas wash-bottle containing nitric acid. This was tested for mercury, and a distinct test could be obtained in every case. Because of the constancy of this loss over a wide range of conditions, it was considered justifiable to apply a correction for it; this correction, calculated from the average of twelve analyses, is +1.3 mg. The results corrected for volatility in this manner are quite accurate, the error seldom exceeding 0.1%.

Stannous Chloride Reduction.—The determination of mercury by reduction to metal with stannous chloride was described as early as 1839 by Rose.[11] More recently it was used by Farup[12] and by Schumacher,[13] who filtered mercury on a gold-asbestos filter, but the method has been unfavorably criticized and little used. Thus Fresenius[14] finds that "this method gives accurate results only when conducted with the greatest care. In general, a little mercury is lost," while Howard[15] states that "stannous chloride is not at all a suitable reducing agent for the estimation of mercurial salts, as the reduction takes place very slowly and is apt to give variable results."

In this work the conditions were found under which this method gives accurate results. Using a large excess of stannous chloride, in a strongly acid solution, the reduction was found to be strictly quantitative and practically instantaneous, the precipitate was easy to filter and the results were accurate both in pure mercuric chloride solution and in the presence of nitrate, sulfate, iron, lead, cadmium, copper, antimony or bismuth.

TABLE III

DETERMINATION OF MERCURY BY REDUCTION WITH STANNOUS CHLORIDE IN AN ACID SOLUTION

No.	$HgCl_2$, g	Mercury, g			Error, mg	Remarks
		Found	Corrected	Calcd.		
1	1.7002	1 2544	1.2554	1.2559	−0.5	
2	1.1585	0.8548	0.8558	0.8558	.0	
3	1.0748	,7931	7941	7939	+ 2	
4	0.9876	.7285	,7295	,7295	.0	
5	.7893	.5824	5834	.5830	+ .4	
6	,6824	.5028	.5038	5041	− .3	
7	.5968	.4399	,4409	.4408	+ .1	
8	,3765	.2773	,2783	.2781	+ .2	
9	,3334	.2457	,2467	2463	+ 4	
10	,1998	.1466	.1476	.1476	.0	
11	1.1073	.8165	8175	.8180	− .5	0.5 g. Fe, 0 9 g. SO_4
12	0.7123	.5256	5266	.5262	+ .4	.1 g. Pb
13	0 8523	6285	6295	6296	− .1	.5 g. Cd
14	1.0616	7836	,7846	,7842	+ .4	.25 g. Bi, 0.22 g. NO_3
15	1 2234	9026	.9036	.9037	− .1	.1 g. Cu, 0 15 g. SO_4
16	1 2272	.9056	.9066	.9065	+ .1	.05 g. Cu, 0 08 g. SO_4
17	1 1930	,8809	.8819	.8818	+ .1	.25 g. Sb
18	1.3989	1.0328	1 0338	1.0334	+ 4	.1 g. Sb

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[11] Rose, "Handbuch des anal. Chem.," 2d ed., 1839, Vol. II, pp. 169–172.

[12] Farup, *Arch. expt. Path. Pharm.*, 44,272 (1900).

[13] Schumacher, *Z. anal. Chem.*, 39, 12 (1900).

[14] Frescnius, "Quant. Chem. Anal.," translation of the 6th German ed. by Cohn, John Wiley and Sons, New York, 1904, Vol. I, p. 366.

[15] Howard, *J. Soc. Chem. Ind.*, 23,151 (1904).

The preferred procedure is as follows: to 50 cc. of the cold neutral solution add 25 cc. of concentrated hydrochloric acid and 5 cc. of freshly filtered stannous chloride solution, containing 1.125 g. of $SnCl_2 \cdot 2H_2O$ per cc., dissolved in hydrochloric acid (sp. gr. 1.09) and kept over metallic tin. Stir and let settle (or centrifuge). Settling is usually complete in thirty minutes to an hour. Filter through a filtering crucible, previously dried with acetone and dry air, wash with 1:1 hydrochloric acid to prevent hydrolysis of tin salts, then with water and finally with acetone. Dry for five minutes by sucking through the crucible air dried by calcium chloride and weigh. The volatility correction in this method, determined from the average of twenty analyses, is +1.0 mg.—somewhat lower than in the hydrazine method. This may be due to the larger size of the particles. The results are shown in Table III.

Summary

1. Conditions are given for the accurate gravimetric determination of mercury after reduction to metal by hydrazine in ammoniacal solution or by stannous chloride in hydrochloric acid solution.
2. In the latter method iron, cadmium, bismuth, copper, lead, antimony, nitrate and sulfate do not interfere.
3. There is always a definite constant loss due only to volatilization of mercury during filtration and drying, for which an accurate correction can be made.
4. A rapid method of drying is described, using acetone and dry air.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 1]

THE SODIUM PEROXIDE–CARBON FUSION FOR THE DECOMPOSITION OF REFRACTORIES

BY GEORGE G. MARVIN WITH WALTER C. SCHUMB

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The usual methods for decomposing refractory materials are far from being ideal, in that they require considerable manipulatory skill, are time-consuming, and frequently do not effect complete decomposition in a single treatment; in fact, for some commercial refractories several types of fusions must be used in succession to obtain this result. Alkaline and acid fusions are frequently carried out in platinum crucibles, entailing considerable expense where a number of analyses must be carried on at once, while nickel, iron or porcelain crucibles are usually badly attacked under similar circumstances. The temperatures obtainable in a fusion are in general limited to those furnished by a gas flame or an electric heating element, commonly not above 1100°. In view of these considerations, a method of fusion which would eliminate some of the objections mentioned is desirable.

Sodium peroxide has been used in the decomposition and analysis of organic compounds for a number of years.[1] In 1925 W. F. Muehlberg[2] described "An Explosion Method for Peroxide Fusion," which showed great possibilities. The metal crucibles would last indefinitely and a number of samples could be fused nearly simultaneously and with a minimum of effort. The cooled melt separated from the crucible very readily and its acidified solution was always clear. The application of the method to the analysis of ferrosilicon was outlined. In a private communication Mr. Muehlberg kindly suggested several lines of further investigation; namely, that aluminum oxide and corundum might be studied with a view to extending the possibilities of this type of fusion. Previous to the work of Muehlberg, we have found no reference to the use of sodium peroxide with sugar carbon for the decomposition of inorganic compounds. From a quantitative aspect it seemed desirable to investigate the efficacy of this method of fusion in the case of a variety of highly refractory materials, such as alundum, cassiterite, zircon, rutile, beryl, mullite, carborundum, graphite, etc.

The following method of study was adopted: (1) to prepare a series of mixtures of sodium peroxide with sugar carbon in varying proportions, and after explosion of these mixtures to determine, if possible, the most advantageous ratio of the components; (2) to use this mixture with an analyzed sample of a refractory material; to vary the proportion of fusion mixture to sample in an effort to determine the proper ratio of mixture to sample, as well as the proper method of mixing, and to determine the amount of unfused residue in each case; (3) to try other organic substances in place of sugar carbon; (4) to fuse a variety of highly refractory materials and in each case to determine the amount of unfused residue, as well as to determine whether or not the unfused material is changed, *i. e.*, whether or not there is any selective action by the sodium peroxide; (5) to determine the maximum temperatures obtained in the case of representative fusions.

Experimental Work

An aluminum tray 12 × 6 × 1 inches was prepared for cooling the crucibles after a fusion. Fitting over the top of this tray was a metal plate with six holes, $1^5/_8$ inches in diameter. A 60-cc. nickel crucible placed in one of the holes would be held firmly in position while resting on the bottom of the tray. Cold water was allowed to run into the bottom of the tray and overflowed at the top.

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[1] In particular, by Pringsheim, *Ber*, **36,** 4244 (1903); von Konek, *Z. angew. Chem.*, **16,** 516 (1903); Pringsheim, *Chem. News*, 91, 215 (1905); Parr, *J. Ind. Eng. Chem*, **14,** 681 (1922); Hein, Hoyer and Klar, *Z. anal. Chem.*, **75,** 161 (1928).

[2] Muehlberg, *Ind. Eng. Chem.*, **17,** 690 (1925).

To obtain a uniform sample of sodium peroxide, the contents of six cans of approximately 150 g. each were thoroughly mixed and placed in glass-stoppered bottles. The purity of the sodium peroxide was tested by acidifying with hydrochloric acid and dehydrating to determine silica. A 15-g. sample thus yielded a residue of 0.003 g.

The sugar carbon used was from Eimer and Amend, bearing the note "prepared from cane sugar." It was somewhat lumpy and was ground in an agate mortar until it passed through a 100-mesh screen. It was noted that when the carbon had been ground to about 50-mesh it assumed a flaky character, resembling that of graphite. This condition made subsequent grinding a tedious operation. Using an automatic grinding apparatus, about 200 g. of 100-mesh carbon was prepared. The purity of the sugar carbon was tested by the ignition of several 2-g. samples in a muffle furnace, addition to the residue of a mixture of sulfuric and hydrofluoric acids, evaporation and ignition. Three samples thus gave residues after the first ignition of 0.0041, 0.0041 and 0.0044 g., respectively. These residues proved to be practically pure silica when subjected to the hydrofluoric acid treatment.

Seven mixtures of sodium peroxide and sugar carbon were prepared, containing, for each 150 g. of peroxide, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0 and 11.0 g. of carbon, respectively. In a preliminary experiment 15 g. of each of these mixtures was fired under identical conditions with no added substance present, the method of firing being as follows. The mixture was weighed into a 60-cc. nickel crucible, then tamped down gently with a glass rod flattened at one end. The crucible was placed iii the metal trough with cold tap water circulating in it, and the mixture was fired by means of the glowing end of a piece of cotton string, inserted through a small hole in the cover of the crucible. The speed of the combustion process increased with increasing proportion of carbon present in the mixture from a slow, but complete combustion, to a very rapid one. The solid mass left in the crucible after the fusion was readily transferred from the crucible to a beaker by tapping and about 60 cc. of cold water was added. After the resulting reaction was complete, the solution was diluted to about 300 cc., cooled, acidified with hydrochloric acid and filtered; the residue was washed with hot water, ignited and weighed. The residues so obtained from the seven mixtures, run in duplicate, varied from 0.0006 to 0.0015 g., and no one of the mixtures could be said to be superior to any other.

In order to determine which of the fusion mixtures was most satisfactory for general use, an analyzed sample of feldspar prepared by the Bureau of Standards and marked "sample 70" was selected, particularly because of its high silica content (66.66% SiO_2), and because it was not especially difficult to decompose. A one-gram sample of this feldspar was mixed with 15 g. of each of the fusion mixtures, care being taken to prevent the sample from coming into contact with the sides of the crucible. This was accomplished by transferring the weighed sample into a conical depression made in the fusion mixture and carefully stirring the sample and fusion mixture with a small spatula, while not disturbing the lining on the sides of the crucible. The entire crucible contents were finally tamped down with the flattened end of a glass stirring rod. On ignition of the seven samples thus prepared, the first three, containing the lowest proportions of sugar carbon, were found unsatisfactory because the reaction was too slow and incomplete; the seventh was discarded as being too rapid for personal safety. The range of mixtures was thus narrowed to the fourth, fifth and sixth, and while no considerable difference in the behavior of these three was noted, Mixture 6, containing 1.50 g. of sodium peroxide to 10.0 g. of sugar carbon was adopted for later use as being the most satisfactory from the point of view of completeness and speed of reaction and ease of preparation.

In the treatment of the contents of the crucible after fusion with water and subsequently with hydrochloric acid, in each case a large quantity of silicic acid gel formed, the filtration of which in the usual way would have been tedious. To obviate this difficulty, the following expedient was employed. After the usual 60 cc. of cold water had been added to the fusion product to decompose the unchanged sodium peroxide, water was added to a volume of about 400 cc. and the whole allowed to stand; after settling, the supernatant liquid was decanted and the solution again diluted to 400 cc. and allowed to settle. After the fourth decantation the solution was acidified and filtered, and the residue washed, ignited in platinum and weighed. Much time was saved by this procedure, inasmuch as the greater part of the sodium silicate had been eliminated before the solution was acidified, thus eliminating the necessity of filtering a gelatinous precipitate. In three typical fusions, using one gram of feldspar with 15 g. of fusion mixture, by the above treatment, residues of 0.0079, 0.0087 and 0.0073 g. were obtained upon ignition. To each of these in platinum crucibles a few drops of concentrated sulfuric acid and about 1 cc. of hydrofluoric acid were added, the whole evaporated to dryness and ignited. Losses of 0.0024, 0.0040 and 0.0015 g., respectively, were observed, thus indicating that the greater part of the unfused residues consisted of undecomposed feldspar.

This conclusion was wholly confirmed by examination of the residues obtained above, as well as the original sample, with a petrographic microscope; the unfused material showed the typical twinning of crystals of feldspar, and possessed the same refractive index as the original material. Whereas the grains of the original material showed sharp broken edges, the grains of the unfused residue had rounded ends with no sharp edges, indicating that incipient fusion by the sodium peroxide treatment had occurred.

It was now obviously a question of determining how best to reduce the amount of unfused residue to a minimum. First, very thorough grinding of the sample in agate was tried, until all the sample would pass through bolting cloth, approximately 100-mesh. The amount of residue obtained from a one-gram sample after fusion and subsequent treatment as already described—0.0082 g.—showed that grinding alone would not suffice to bring about complete fusion.

Various expedients were tried in modifying the method of mixing the sample and fusion mixture, both within and outside the crucible, and the ratio of mixture to sample was raised to 25:1, but the unfused residues remained unsatisfactorily large, until it was discovered that the cause of the large residues was due to spattering of material during fusion on to the sides and cover of the crucible. Thus, it was found, when the spattered material and the solid fused mass in the crucible were separately treated after fusion, that approximately 80% of the residue came from the spatterings, the rest—about 1 mg.—from the solid lump. The spattering could not be eliminated entirely by any of the several expedients tried, although a covering of about 5 g. of sodium carbonate applied to the contents of the crucible before firing was found to reduce this considerably. Thus, using a one-gram sample of feldspar in the usual method of procedure, but employing the sodium carbonate covering, three samples gave residues as follows: (a) from the solid mass in the crucible, 0.0004, 0.0008 and u.0005 g.; and (b) from the spatterings, 0.0038, 0.0024 and 0.0021 g., respectively.

Several mixtures of organic compounds with sodium peroxide were tried with a view to determining whether or not the carbon might be replaced by a compound, and the necessity of grinding the carbon thus eliminated; but of the substances tried, in varying proportions, with the peroxide—benzoic acid, oxalic acid and tartaric acid—none gave as satisfactory results as the ground sugar carbon. It is possible that certain pure, solid hydrocarbons, such as triphenylmethane, would prove to be satisfactory substitutes for the carbon, but further work along these lines was not attempted.

It was thought desirable to determine, at least approximately, the maximum temperature attained in this method of fusion. For this purpose the use of a thermocouple or optical pyrometer seemed impracticable, as the high temperature obtained lasts but a few seconds. Strips of silver foil and copper foil melted readily in the fusion mixture so that a temperature of at least 1100° was indicated. By the use of flake graphite in place of sugar carbon the combustion progressed more slowly, requiring about thirty seconds for completion, so that an optical pyrometer could be employed. With this instrument typical fusion mixtures on firing showed temperatures of approximately 1-1-50". It seems probable that with the faster burning charcoal temperatures considerably in excess of this are attained.

The following highly refractory materials, after grinding in agate, were now fused in succession, employing the usual procedure outlined above: 1, fused kaolin brick; 2, ignited crucible, largely zirconium oxide; 3, sipylite, chiefly erbium columbate; 4, commercial product of fused alumina and magnesia; 5, commercial product of fused alumina and silica; 6, alundum; 7, cassiterite; S, corundum; 9, rutile; 10, zircon concentrates; 11, beryl; 12, ilmenite; 13, mullite, a commercial product of fused alumina and silica; 14, carborundum; 15, flake graphite.

In certain cases grinding of the sample to 100-mesh was found desirable, so that residues of only a few milligrams should result after fusion and subsequent treatment. For example, one-gram samples of alundum and corundum gave the following residues.

		Without careful grinding of sample, g.	Sample ground to pass 100 mesh, g.
I Alumina	Residue from fusion	0.0020	0.0016
	Residue from spattering	.0020	.0005
II Corundum	Residue from fusion	.0073	.0010
	Residue from spattering	.0058	.0004

In nearly all cases, when careful grinding was employed, the total residue obtained from a one-gram sample did not exceed 0.0025 g. and was usually much less than this.

In the case of the carborundum sample, the procedure was modified in order that the reaction might not be too violent. About 10 g. of fusion mixture was placed in the bottom of the crucible and above it 10 g. of sodium peroxide was introduced, into which the 0.5-g. sample of carborundum (100-mesh) was stirred. The whole was covered with about 5 g. of fusion mixture and fired. The results obtained were very satisfactory.

In the case of the graphite, the sugar carbon was entirely omitted and the one-gram sample mixed directly with 15 g. of sodium peroxide. The residue after acidification was filtered through a Gooch crucible instead of being ignited in the muffle furnace, since in the latter the graphite residue was observed to burn down to an ash.

The fact that the sodium peroxide–carbon fusion does not have a selective action on the refractories studied was determined by microscopic examination of the crystal grains, before and after fusion. For example, Sample 13, mullite, before and after fusion gave the appearance seen in the photomicrographs. Before fusion the grains were not uniform in size and showed sharp edges—in the sample shown in the photomicrograph the smaller grains were washed away by decantation and only the larger ones remained; after fusion, the fragments of residue obtained were more nearly uniform in size and the edges appeared rounded—in preparing the photograph of the fused material the decanting of the lighter particles was not carried out. Consequently, the fusion appears to have entirely consumed the smallest particles and uniformly eroded the surfaces of the larger ones—facts that indicate no selective action on the part of the fusion medium. In calculating the results of an analysis, it, therefore, would seem to be justifiable merely to subtract the weight of residue from that of the original sample.

Before fusion.

After fusion.

Summary

A quantitative study of the sodium peroxide–carbon method of fusion has been made in the case of fifteen highly refractory materials, including both naturally occurring minerals and artificial products. The results show that, properly executed, this fusion may well replace any of the customary methods for the decomposition of refractories, being more complete in many cases, and far superior in point of speed and ease of manipulation; being carried out in nickel, it obviates the need of platinum crucibles. No loss in weight of the nickel crucible is detected after repeated use.

Details are given for the proper method of procedure in preparing the sample and the fusion mixture, as well as the proper proportions of mixture to sample, the mode of charging, firing and cooling the crucible and the subsequent treatment of the fusion product.

It is shown that the unfused residue from a one-gram sample, ground to at least 100-mesh, need not exceed two milligrams, and that this small residue consists of particles of the original sample and, therefore, may be subtracted from the original weight.

Cambridge, Massachusetts

[CONTRIBUTION FROM THE GOVERNMENT COLLEGE CHEMICAL LABORATORIES]

ACTION OF SULFURIC ACID ON TMIOCYANATES

BY B. S. SHARMA

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Thiocyanic acid can be prepared by the action of dilute sulfuric acid on alkali thiocyanates, with subsequent distillation under reduced pressure, collecting the distillate in a receiver kept in a freezing mixture.[1] At ordinary room temperature RSCN polymerizes to $(HCNS)_2$ and $(HCNS)_3$. With dilute sulfuric acid persulfocyanic acid, $H_2C_2N_2S_3$, is obtained. Decomposition with sulfuric acid is represented as

$$\text{(Dilute sulfuric acid)}\ 2HSCN + 2H_2O \longrightarrow 2NH_3 + CS_2 + CO_2$$
$$\text{(Strong sulfuric acid)}\ HCNS + H_2O \longrightarrow COS + NH_3$$

Persulfate and other oxidizing agents, according to Pawlewsky[2] and Goppelsroeder,[3] with thiocyanates yield $C_3N_3S_3H$. Concentrated sulfuric acid[1c] acts vigorously with solid thiocyanates and evolves acrid vapors consisting of formic acid, sulfur dioxide and carbon dioxide, and sulfur separates out.

While estimating the composition of the precipitate formed by treating ammonium thiocyanate solutions with sulfuric acid, it has been noticed that the composition of the precipitate varies according to the strength of ammonium thiocyanate and sulfuric acid solutions used. It has also been noticed that the stronger the sulfuric acid used, the lower became the sulfur content of the precipitate. The reaction of concentrated sulfuric acid on thiocyanates described by Allen does not seem to take place when solid ammonium thiocyanate is treated with concentrated sulfuric acid in the cold.

Anal. Calcd. for $H_2C_2N_2S_3$: C, 16; H, 1.3; N, 18.7; S, 64.0. Calcd. for $C_3N_3S_3H$: C, 20.6; H, 0.6; N, 24.0; S, 54.9.

Experimental

The composition of the precipitates obtained by using solutions of different strengths of ammonium thiocyanate and sulfuric acid was found to vary as follows—C, 13.01 to 17.6; H, 0.9 to 2.8; N, 18.4 to 21.3; S, 57.0 to 65.5.

The precipitate obtained by using a saturated solution of ammonium thiocyanate and 20% sulfuric acid in equal quantities gave the following results—C, 15.9 to 15.95; H, 1.01 to 1.1; N, 19.0 to 20.3; S, 62.5 to 65.5.

The precipitate obtained by treating solid ammonium thiocyanate

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[1] (a) Kalason, J. *prakt. Chem.*, II, **36**, **57** (1887); **(b)** *ibid.*, **38**, 383 (1888); (c) Allen, "Technical Analysis," Vol. VII, p. 544.

[2] Pawlewsky, *Ber.*, **33**, 164 (1903).

[3] Goppelsroeder, **J.** Chem. *Soc.* (Abstracts), **48**, 109 (1885).

with 50% sulfuric acid with gentle heating gave as analytical results—C, 16.4 to 16.5; H, 0.76 to 1.1; N, 19.2 to 20.0; S, 57.0 to 57.0.

Some of the precipitates were found to leave a little residue on combustion (mostly of iron oxide).

When solid ammonium thiocyanate was treated with concentrated sulfuric acid in the cold, a white precipitate was formed which was not sulfur. It dissolved after a few days, producing a sirupy liquid which did not give the characteristic red coloration with ferric chloride.

Concentrated hydrochloric acid produced a yellowish-white precipitate. It dissolved in water and the solution became turbid on heating.

All attempts to obtain these precipitates in a pure state have failed.

The acids used were Kahlbaum's pure reagents.

Discussion.—The analytical results show that the precipitates obtained by treating ammonium thiocyanate with sulfuric acid are generally mixtures of varying composition, depending on the strength of ammonium thiocyanate and sulfuric acid used. A study of the sulfur and carbon results shows that sulfuric acid has a variable oxidizing influence on thiocyanates, depending on the strength of acid used.

This work has been carried out at the Government College Chemical Laboratories, Lahore, India. Thanks are due to Dr. Dunnicliff for suggesting the problem.

Conclusions

1. The thiocyanate-sulfuric acid precipitates are generally mixtures.
2. There seem to be two factors which influence the formation of the precipitate: the strengths of (a) the ammonium thiocyanate solution and (b) of the sulfuric acid.
3. Sulfuric acid, besides its hydrolyzing effect, appears to have an oxidizing influence on thiocyanates; the stronger the acid the more marked is the effect.

LAHORE, INDIA

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

POTENTIOMETRIC TITRATIONS OF PHOSPHATES, ARSENATES AND ARSENITES WITH SILVER NITRATE[1]

BY M. HUME BEDFORD, FRANCES ROBERTS LAMB AND W. EDWARD SPICER

RECEIVED SEPTEMBER 21, 1929 PUBLISHED FEBRUARY 6, 1030

Introduction

Neither Treadwell and Weiss[1a] nor Pinkhoff[2] were able to carry out the potentiometric titration of phosphates and arsenates with silver nitrate. Kolthoff and Furman[3] suggest the use of a buffer solution to keep the hydrogen-ion concentration low enough to cut down the solubility of the silver phosphate and arsenate.

In this investigation various salts of weak acids and stronger bases were used as buffers with varying degrees of success. However, successful results were obtained by using a 0.1 N solution of sodium or potassium hydroxide for a secondary titration to keep the solution at a constant hydrogen-ion concentration. This method gave consistent results with alkali phosphates, arsenates and arsenites and with phosphate rock and arsenate insecticide.

By using a Leeds and Northrup student potentiometer the potentials were measured between silver and normal calomel electrodes.

Materials

Approximately 0.1 *N* solutions of $AgNO_3$, $NaNH_4HPO_4$, Na_2HAsO_4, Na_2HAsO_3, and NaH_2PO_4 were made and standardized. The $AgNO_3$ solution was standardized by electrolytically depositing the silver;[4] the $NaNH_4HPO_4$ by using a definite weight of the salt; the Na_2HAsO_4 by precipitation and weighing as Ag_3AsO_4;[5] the Na_2HAsO_3 by using a definite quantity of As_2O_3; the NaH_2PO_4 by precipitation and weighing as magnesium pyrophosphate.[6]

Experimental

Sodium bicarbonate[3] and ammonium acid succinate were tried as buffer solutions to neutralize the nitric acid formed during the titration.

$$Na_2HAsO_4 + 3AgNO_3 = Ag_3AsO_4 + 2NaNO_3 + HNO_3$$

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[1] An abstract of theses submitted in partial fulfilment of the requirements for the Degrees of Master of Science at the University of Kentucky, 1928 and 1929.

[1a] Treadwell and Weiss, *Helv. Chim. Acta*, **2**, 680 (1919).

[2] Pinkhoff, "Over de Toepassing der Elektrometrische Titraties," Dissertation, Amsterdam, **1919.**

[3] Kolthoff and Furman, "Potentiometric Titrations," John Wiley and Sons, Inc., New York, **1926**, p. 179.

[4] Edgar F. Smith, "Electro-analysis," P. Blakiston's Son and Co., Philadelphia, **1907**, p. 107.

[5] Georg Lunge and Arnest Berl, "Chemisch-technische Untersuchungsmethoden," 6th ed, **1910**, p. 716.

[6] Treadwell and Hall, "Analytical Chemistry," Vol. II, Quantitative Analysis, John Wiley and Sons, Inc., New York, **1924**, p. 379.

However, silver succinate and silver carbonate seemed to be precipitated and end-points were not obtained. The titration curve showed a break corresponding to excess silver nitrate or silver in solution when the small amounts of nitric acid resulting from the reaction were successively neutralized with 0.1 N sodium hydroxide, using one drop of 0.1 N phenolphthalein indicator to each 50 cc. of solution. This suggested the use of sodium phenolphthalate as a buffer. In this case the titration curves showed breaks, but varying end-points were observed with different amounts of the buffer.

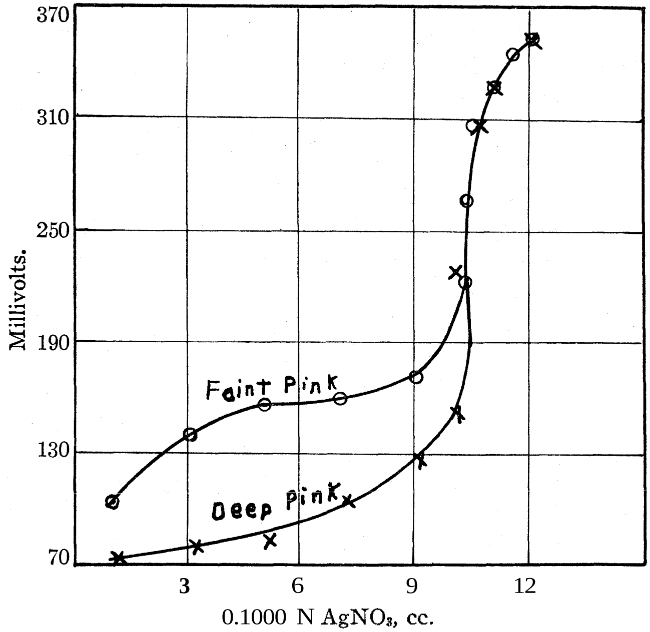

Fig. 1.—Titration curves of two portions of the same solution, one titrated with NaOH until the color of the solution due to the indicator was faint pink; the other until the color was deep pink.

The remaining experimental work was restricted to the use of sodium hydroxide for a secondary titration to the alkaline reaction. The use of the additional buret offered no disadvantage or difficulty. It was not necessary to record the readings of this buret. The solution containing the silver phosphate or arsenite could be neutralized without discontinuing the stirring of the solution. However, as the color of the silver arsenate precipitate is a brick-red, the stirring of the solution was stopped occasionally and the precipitate allowed to settle to make certain that the liquid itself retained a rose-pink color. The volume of the titrated solution was always kept under 300 cc.

Since the question might arise as to whether the sodium hydroxide solution should be added until the phenolphthalein assumed a faint or a deep pink color, the effect on the potential of small variations in the quantity of sodium hydroxide used was studied at different intervals in the titration. While even one drop of 0.1 N sodium hydroxide produced considerable change in the potential before the end-point was reached, the effect of an equal quantity immediately after the end-point had been passed was negligible (Pig. 1).

TABLE I

EFFECT OF SODIUM HYDROXIDE AFTER END-POINT

	Arsenate	Arsenite	Phosphate
Initial potential, v.	0.309	0.340	0.3060
After 1 drop 0.1 N NaOH, v.	.309	.340	.3060
After 2 drops 0.1 N NaOH, v.	.309	.340	.3055
After 3 drops 0.1 *N* NaOH, v.	.308	.339	.3045

Also, in this connection a comparative study was made of the total quantity of silver nitrate required for the various substances when the color of the solution was a faint or a deep pink.

TABLE II

EXPERIMENTAL RESULTS

	Sample, cc.	$AgNO_3$, cc. (faint pink)	$AgNO_3$, cc. (deep pink)
Arsenate	25	25.28	25.33
Arsenite	10	10.08	10.09
Phosphate	10	10.40	10.40

Three slight variations of the drop method were compared. The first variation consisted of adding silver nitrate drop by drop and neutralizing the solution with very dilute (0.01 N) sodium hydroxide after

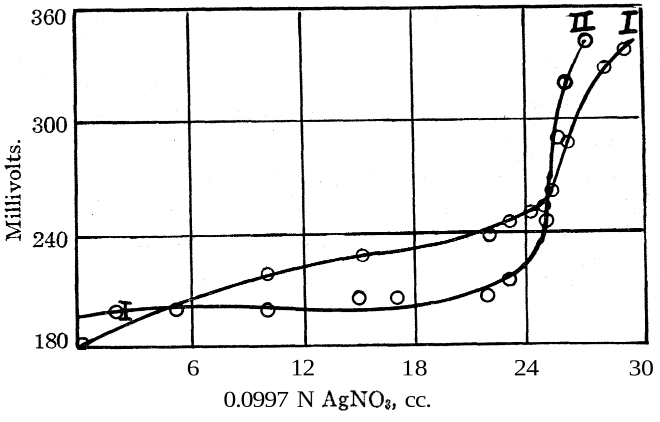

Fig. 2,—Titration curves: I, 25 cc. of 0.1031 N NaH_2PO_4; II, 25 cc. of 0.1011 N $NaHAsO_4$.

each one or two drops. The second required the addition of a drop of silver nitrate followed by a drop of 0.07 N sodium hydroxide. In the third, sodium hydroxide was present in excess before the addition of silver nitrate by drops so that no more sodium hydroxide had to be added.

TABLE III
EXPERIMENTAL RESULTS

(a) Very faint pink solution 0.01 N NaOH

$AgNO_3$, cc.	Potential, mv.	dE/d cc.
8.95	201	
		3
9.95	204	
		10
10.05	205	
		640
10.10	237	
		460
10.15	260	
		130
10.20	273	

Maximum dE/d cc., 10.08 cc.

(b) One drop of $AgNO_3$; one drop of 0.07 N NaOH

$AgNO_3$, cc.	Potential, mv.	dE/d cc
9.94	140	
		575
9.98	163	
(after 1 drop NaOH)	141	
		900
10.03	186	
(after 1 drop NaOH)	150	
		1780
10.08	239	
(after 1 drop NaOH)	238	
		520
10.13	264	
(after 1 drop NaOH)	264	
		300
10.16	279	

Maximum dE/d cc., 10.06 cc.

(c) Deep pink when first drop of $AgNO_3$ added

$AgNO_3$, cc.	Potential, mv.	dE/d cc.
9.45	109	
		84
9.95	151	
		200
10.01	163	
		967
10.07	221	
		732
10.12	265	
		233
10.18	279	

Maximum dE/d cc., 10.04 cc.

The results obtained by the potentiometric method have been compared with the results obtained by the standard methods (Table V). In the tables the first column contains the results obtained when using the calculated equivalence potential; the second column, when using the drop method; the third, when using the experimentally determined equivalence potential. The equivalence potentials for these first columns were determined from the solubility products, using the formula[7]

$$E = e_0 - 2.303\frac{RT}{NF(x + y)}\left(P_{S_{B_xA_y}} - \log\frac{x}{y}\right)$$

where $e_0 = 0.798$ volt for the silver electrode; $T = 294°$ absolute, room temperature; $x = 3$ and $y = 1$, since $xB^{n+} + yA^{m-} = B_xA_y$.

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[7] Ref. 3, p. 71.

TABLE IV

EQUIVALENCE POTENTIALS

	Ag_3PO_4	Ag_3AsO_4	Ag_3AsO_3
Solubility (g. per liter water 20°)	6.4×10^{-3}[a]	8.5×10^{-3}[b]	11.5×10^{-3}[b]
Concn. Ag ion, equiv. per liter	4.61×10^{-5}	5.53×10^{-5}	7.73×10^{-5}
Solubility product	1.54×10^{-18}	3.12×10^{-18}	1.2×10^{-17}
P_s	17.812	17.506	16.923
E (against normal hydrogen elect.)	0.5450	0.5502	0.5579
E of N calomel elect.	0.2871	0.2871	0.2871
E (against N calomel elect.)	0.2579	0.2631	0.2708

[a] Wilhelm Böttger, *Z. physik. Chem.*, 46, 603 (1903). [b] G. Stafford Whitby, *Z. anorg. Chem.*, **67,** 108 (1910).

Two sets of determinations were made with the microcosmic salt, the second of which was titrated after being boiled with sodium hydroxide. The difference in results is such as might be expected due to the presence of the ammonium group.

TABLE V

RESULTS OF EXPERIMENTS

Sample taken, cc.		% Error in comparison with standard values when the end-point was determined by		
		Calcd. potential	Drop method	Experimental potential
Na_2HAsO_4	10	0.4	0.3	0.5
	25	0.2	0.1	0.3
Na_2HAsO_3	10	1.1	0.3	0.4
	25	0.4	0.0	0.0
	50	0.5	0.0	0.2
NaH_2PO_4	10	−0.8	1.0	1.2
	25	−1.4	0.8	0.7
$NaNH_4HPO_4$	10	1.0	7.2	7.6
	25	0.3	6.9	7.0
$NaNH_4HPO_4$ (boiled with NaOH)	10	−0.7	1.5	1.5
	25	−0.8	1.7	0.7

A rough comparison between the actual quantities of sodium hydroxide required completely to neutralize the nitric acid formed by the reaction and the theoretical quantities has been made. This comparison shows that a relatively large amount of the sodium hydroxide is used in replacing the ammonium group.

TABLE VI

0.1 *N* SODIUM HYDROXIDE USED FOR 25 CC.

	Experimentally, cc.	Calculated, cc.
0.1011 *N* Na_2HAsO_4	9.2	8.7
0.1000 *N* Na_2HAsO_3	24.7	8.3
0.1000 *N* $NaNH_4HPO_4$	13.3	8.3
0.1000 *N* $NaNH_4HPO_4$ (boiled with NaOH)	18	16.7
0.1031 *N* NaH_2PO_4	18.3	16.7

Since excess sodium fluoride does not interfere with the precipitation of silver arsenate,[8] the calcium in samples of phosphate rock and calcium arsenate insecticide was precipitated with excess sodium fluoride (4%) and the phosphate and arsenate titrated with silver nitrate. In this procedure the nitric acid solution of the calcium phosphate or arsenate was neutralized with sodium hydroxide to the point at which the precipitate just barely redissolved, then the excess sodium fluoride was added and the titration started with silver nitrate. Before the addition of alkali, readings were made until a potential of approximately 0.24 volt was reached, then the sodium hydroxide was added to produce the pink color and the titration continued. By this method all the calcium was precipitated as calcium fluoride instead of calcium phosphate or calcium arsenate and results were obtained which agreed with those from standard methods of analysis of the same samples.

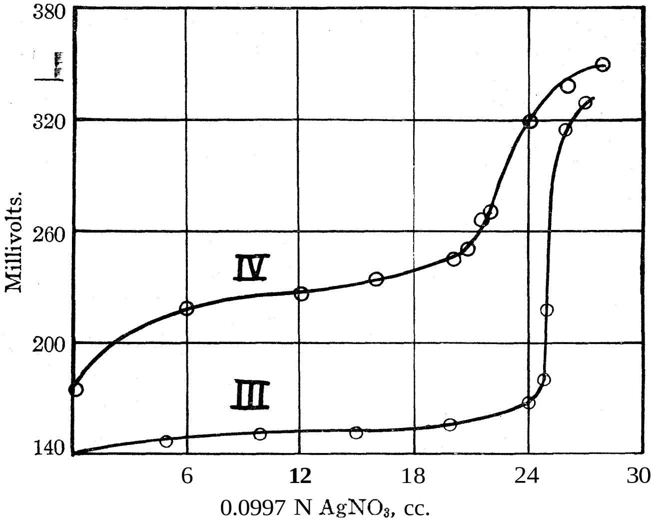

Fig. 3.—Titration curves: III, 25 cc. of 0.1000 *N* Na_2HAsO_3; IV, 20 cc. of 0.1000 N $NaNH_4HPO_4$.

Summary

The potentiometric titration of phosphates, arsenates and arsenites with silver nitrate has been accomplished by making use of a secondary titration with sodium hydroxide to maintain the desired low hydrogen-ion concentration. The phosphate titration proved the least satisfactory.

LEXINGTON, KENTUCKY

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[8] LeRoy W. McCay, THIS JOURNAL, **50,** 368 (1928).

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

THE POTENTIAL OF LEAD–LEAD ION

BY MERLE RANDALL AND JESSIE Y. CANN

RECEIVED SEPTEMBER 23, 1929 PUBLISHED FEBRUARY 6, 1930

The potential of the lead–lead ion electrode was taken as 0.122 volt by Lewis and Randall,[1] who based their calculations largely upon measurements of the lead–lead chloride electrode and a fairly satisfactory guess of the activity coefficient of lead chloride in the saturated solution. New methods of evaluating the activity coefficients, new values of the reference electrodes and the results of the solubility measurements of Randall and Vietti[2] make it desirable to restudy the older measurements and to determine the potential by an independent method.

The Cell: Pb (in sat. amalg.), $Pb(NO_3)_2$ (aq) | KNO_3 (aq) | KC1 (aq), AgCl (s), Ag (s).—The activity coefficient of lead nitrate was measured by Randall and Scott[3] by the freezing point method, and since the uncertainty in the potential of the flowing liquid junction with a common ion at the same equivalent concentration of salts is not large, we have measured the cell Pb (in sat. amalg.), $Pb(NO_3)_2$ (aq) | KNO_3 (aq) | KC1 (aq), AgCl (s), Ag (s).

The Cell.—The electrode vessels were of the usual form. The flowing junctions were an all-glass modification of the type described by Randall and Langford.[4] The complete cell of pyrex glass is shown in Pig. 1. The dropping funnels A, B and C contained the solutions of lead nitrate, potassium nitrate and potassium chloride. The reservoirs D, E and F were filled with the corresponding solutions and served to bring the temperature of the solutions to the temperature of the thermostat. During measurements Stopcocks G and H were open and I and J were adjusted so that there would be the same flow from the tips K and L. The flow was regulated by means of the stopcocks of the dropping funnels. The rods M and N were raised, the flow from tips K and L regulated, then the rods were lowered and contact was made through the film of solution around the rods. Waste solutions were continuously removed by means of suction applied to small tubes inserted nearly to the bottom of O and P.

The warmed lead amalgam was poured rapidly in succession through a series of clean, dry, pyrex glass test-tubes, which removed all traces of the slight surface film of oxides, and was immediately introduced into the

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

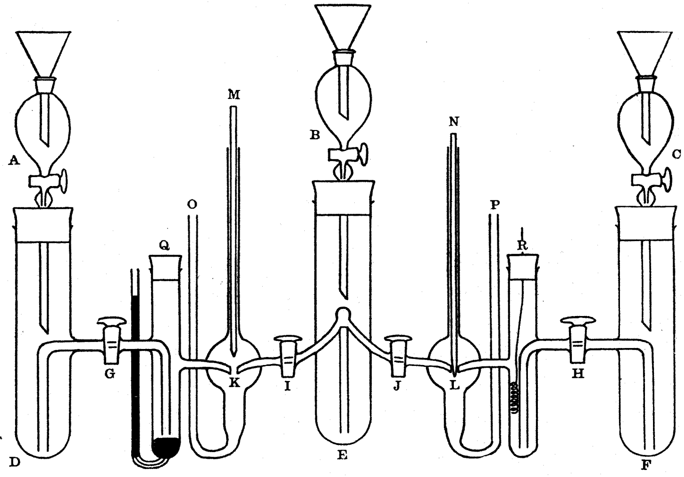
[2] (a) Randall and Vietti, THIS JOURNAL, 50, 1526 (1928); (b) "International Critical Tables," McGraw-Hill Book Co., New York, Vol. VII, Section on Free Energy of Chemical Substances (in press).

[3] Randall and Scott, THIS JOURNAL, 49, 636 (1927).

[4] Randall and Langford, unpublished.

cell, Q, and covered quickly with the solution that was to be used. This was done after the whole apparatus had been flushed with hydrogen. The surface of the amalgam was just below the tip of the connecting tube. The cell was placed in the usual oil thermostat, and measurements were made with a shielded Leeds and Northrup Type K potentiometer.

Materials.—The solutions were made up by weight (moles per 1000 g. of water in vacuum) from high grade "analyzed" salts and conductivity water. Pure hydrogen was bubbled through the solutions to remove traces of oxygen.



Pig. 1.—Cell with two flowing junctions.

The saturated two-phase lead amalgam was made by heating together in vacuum 5 g. of "analyzed" test lead and 100 g. of distilled mercury according to the method of Gerke.[5] This amalgam had a slight film of oxide which was removed as described above.

The silver–silver chloride spiral electrodes were made in the same way as those used by Randall and Young.[6] Before introducing into the electrode vessel, the spirals were placed in the solution to be used and evacuated for about thirty minutes with gentle heating, or until all bubbles ceased to appear at the surface of the spiral. Complete removal of oxygen by the above means and by flushing the solutions and apparatus with hydrogen was found to be necessary in order to obtain steady and concordant potentials.

The Standard Potential of the Lead–Lead Ion Electrode.—The molality of the solutions used and the potentials obtained are shown in the first four columns of Table I.

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

[6] Randall and Young, *ibid.*, 50, 989 (1928).

TABLE I

Pb (IN SAT. AMAL.), $Pb(NO_3)_2$ (AQ.) | KNO_3 (AQ.) | KCl (AQ.), AgCl(s), Ag(s) AT 25°

m Pb-$(NO_3)_2$	m KNO_3	m KCl	E volt	E $Pb(NO_3)_2$ | KNO_3	E KNO_3 | KCl	E less liquid	$E^\circ_{298 \cdot 1}$	$\mu^{1/2}$	log γ + const
0.025	0.05	0.05	0.4760	−0.0062	0.0013	0.4809	0.3361	0.2738	−4.0188
.05	.10	.10	.4545	− .0078	.0017	.4606	.3367	.3873	−4.0910
.10	.20	.20	.4327	− .0098	.0023	.4402	.3368	.5477	−4.1621

The values of the potential given in Col. 4 represent the average of several hundred measurements with various rates of flow of the solutions in the liquid junctions, with several solutions and different electrodes for each series. The flowing liquid junctions proved quite reproducible, the principal error being introduced by alteration of the temperature of the solutions when the rate of flow was great. About forty drops per minute was found to be the best rate. The potentials of the liquid junctions were calculated by means of the Lewis and Sargent[7] formula, the conductivities being taken from the compilation by Holborn[8] from the work of Kohlrausch and others at 18°. The ratio of the conductivities at 18 and 25° was assumed to be the same.

The cell reaction after elimination of liquid potentials may be written

$$\text{Pb(in sat. amalg.)} + 2\text{AgCl(s)} = 2\text{Ag(s)} + \text{Pb}^{++}\,(\text{in Pb(NO}_3)_2\ (\text{aq.}) + 2\text{Cl}^-\ (\text{in KCl (aq.)}) \quad (1)$$

in which, formally, aqueous lead chloride is produced, not with an activity coefficient which is that of lead chloride, but one which is the geometric mean of the activity coefficients of lead and chloride ions in lead nitrate and potassium chloride, respectively. As an approximation, which is not wholly justified, we may assume the hypothesis of the independent activity coefficient of the ions,[9] whence the activity coefficient of this hypothetical lead chloride is given by

$$\gamma_\pm(\text{Pb}^{++}\ (\text{in Pb(NO}_3)_2\ (\text{aq.}))\ 2\text{Cl}^-\ (\text{in KCl (aq.)}) = [\gamma^3(\text{Pb(NO}_3)_2)\ \gamma^4\text{KCl}/\gamma^4\text{KNO}_3]^{1/3} \quad (2)$$

Whence, substituting the values of the activity coefficients taken from the work of Randall and Scott,[3] for lead nitrate, of Randall and White[10] for potassium chloride, and of an unpublished summary of activity coefficients, we find by the usual equation[11] the values of E° given in the eighth column of Table I, from which we choose the average value

$$E^\circ = 0.3367 \text{ v.}; \quad \Delta F^\circ_{298 \cdot 1} = -15{,}538 \text{ cal.}$$

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[7] Lewis and Sargent, THIS JOURNAL, 31, 363 (1909).

[8] Landolt, Bornstein, Roth, Scheel, "Tabellen," Springer, Berlin, 1923, Vol. II, pp. 1079–1080.

[9] Ref. 1, p. 380.

[10] Randall and White, THIS JOURNAL, 48, 2514 (1926).

[11] (a) (Ref. 1, p. 396); (b) Randall, Trans, *Faraday Soc.*, 23, 505 (1927).

We may make an independent extrapolation of the activity coefficient of this hypothetical aqueous lead chloride by means of the equation[11b]

$$\log \gamma + \text{const.} = -\mathbf{E}/0.088725 - \log m^* \tag{3}$$

The values of the square root of the ionic strength and of log γ +const. in Equation 3 are given in the last two columns of Table I. Plotting on transparent paper, log γ +const. on the standard scale against $\mu^{1/2}$ and referring to the standard plot of activity coefficients as was done by Randall and Vietti,[2] we obtain constant = –3.8000 or $\mathbf{E}^\circ$ = 0.3372 v.; but the value 3.7938, corresponding to $\mathbf{E}^\circ$ = 0.3366 seems from the plot to be a reasonable value.

For the potential of saturated lead amalgam we take[12]

$$\text{Pb(s)} = \text{Pb(in sat. amalg.)};\ \mathbf{E}^\circ_{298.1} = 0.00586;\ \Delta F^\circ_{298.1} = -270 \text{ cal.} \tag{4}$$

whence

$$\text{Pb(s)} + 2\text{AgCl(s)} = \text{Ag(s)} + \text{Pb}^{++} + 2\text{Cl}^-;\ \mathbf{E}^\circ_{298.1} = 0.3424\text{ v};\ \Delta F^\circ_{298.1} = -15{,}801 \text{ cal.} \tag{5}$$

and combining with Gerke's value for the free energy of formation of silver chloride (ΔF°_{298}, = –26,220), and the new value of the chloride ion of Randall and Young[7] ($\Delta F^\circ_{298.1}$ = –31,345) we find

$$\text{Pb} = \text{Pb}^{++} + 2E^-;\ \mathbf{E}^\circ_{298.1} = 0.1203 \text{ v};\ \Delta F^\circ_{298.1} = -5551 \text{ cal.} \tag{6}$$

The relation of this potential to that determined from the potential of lead–lead halide electrodes will be discussed in another place.

Summary

The potential of the lead–lead ion electrode has been determined by measurements of the lead amalgam–lead nitrate electrode, combined through flowing junctions, with a silver–silver chloride electrode. The standard potential of lead ion is found to be 0.1203 v., and the free energy of formation to be –5551 cal. at 25°.

BERKELEY, CALIPORNIA

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[12] Randall and Spencer, unpublished, see Ref. 2 b

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

THE TEMPERATURE COEFFICIENT OF THE SYNTHESIS OF HYDROGEN CHLORIDE BY LIGHT AND BY ALPHA-RADIATION

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In 1926, Porter, Bardwell, and Lind[1] compared the rates of hydrogen chloride synthesis by light and by a-rays at 25°. The method consisted in circulating the same mixture of hydrogen and chlorine through a light chamber and through an a-ray chamber, employing in the latter radon in a thin a-ray bulb. The principal result was the discovery that any change in sensitivity of the gas mixture toward one form of activation was exactly the same as for the other. This result is readily interpreted in terms of chain mechanism, as meaning that by no matter what agency a chain is initiated, its further propagation depends only on the gas mixture and its sensitivity (concentration of inhibitors which terminate the chains). This primary result is confirmed in the present work.

The absolute value of the ratio of the yield per ion pair to that per light quantum, which Porter, Bardwell and Lind[1] found equal to nearly 4, has not been wholly confirmed, but a value approximating unity has been obtained. This discrepancy may be partly due to the fact that in the present photochemical experiments a strictly monochromatic source was used for the quantum yield measurements, whereas in the work of Porter, Bardwell and Lind a considerable fraction of the chlorine absorption band was involved. As Allmand and Beesley[2] have recently shown, the different wave lengths absorbed are by no means equal in efficiency in causing synthesis of hydrogen chloride. When correction is made by using Allmand and Beesley's data[2]", the values are reduced from unity and 3.7 to slightly less than unity and to approximately 2.5, respectively. We have at present no explanation for this three-fold discrepancy.

In the paper of Porter, Bardwell and Lind[1] it was found that the photochemical yield per quantum increased about two-fold in the interval 25–100°. On the assumption that the a-ray reaction, in analogy to most of the other reactions previously studied, would be independent of temperature, it was concluded that the M/N and $M/h\nu$ yields might approach each other at high temperatures. Experiment has shown the danger of faulty analogy, since sight was lost of the fact that none of the supposedly analogous a-ray reactions had chain mechanisms, and that if the temperature coefficient is largely determined by the chain part of the reaction, as predicted by Cremer,[3] then the a-ray and light reactions should possess

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[1] Porter, Bardwell and Lind, THIS JOURNAL, 48,2603 (1926).

[2] (a) Allmand and Beesley, Nature, 123, 164 (1929); see also (b) Coehn and Jung, *Z. physik. Chem.*, 110, 705 (1924).

[3] E. Cremer, *ibid.*, 128, 285 (1927).

identical temperature coefficients. The present experiments show this to be the case for white light.

This conclusion must be contrasted with Tolman's[4] theory of the temperature coefficient as a function of the primary rather than the secondary step in the reaction. If each wave length has its own temperature coefficient, the greater the smaller the quantum, then only by accident will any one of these or the average of all coincide with the α-ray temperature coefficient. More drastic comparison with "green light" ($NiSO_4$ filter) over the same temperature range showed a temperature coefficient of 1.3 for a 10° interval, which is distinctly higher than 1.2, the value for white light in the same region of sensitivity. This may mean that Tolman's theory[4] is not incorrect in principle, but that actually the temperature coefficient is determined almost entirely by one or more steps in the chain mechanism rather than in the primary step.

Porter, Bardwell and Lind[1] also found that the temperature coefficient is a function of the sensitivity, becoming greater the higher the sensitivity. This has been confirmed, but their case of an actual negative coefficient at very low sensitivity could not be substantiated. The actual value of the 10° coefficient is higher by about 0.1 than that of Porter, Bardwell and Lind; the maximum is lower than that of Padoa and Butironi[5] for white light, but is in good agreement with the average of Bevan's values.[6]

Apparatus and Calibration

The apparatus used was a modified Bunsen and Roscoe actinometer,?similar to that employed by Porter. Bardwell and Lind[1] The essential part of the apparatus, a diagram of which is given in Fig. 1, are an electrolytic generator, a capillary U-tube trap containing a few drops of water, a magnetic circulating pump, an absorption vessel, two reaction chambers in separate thermostats and a graduated capillary actinometer. The entire apparatus was made of pyrex glass.

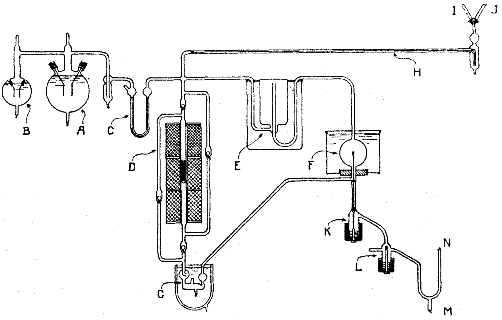

Fig. 1.—Diagram of the apparatus.

The generator **A** contains concentrated hydrochloric acid. The electrodes are of platinum–iridium alloy and are introduced through small rubber stoppers, which are covered outside by mercury seals. The generator B contains dilute sulfuric acid and was used to generate a hydrogen-oxygen mixture, when it was desired to decrease the sensitivity of the gaseous mixture. Since the amount of oxygen added was always a

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[4] Tolman, THIS JOURNAL, **42**, 2506 (1920); **45**, 2285 (1923).

[5] Padoa and Butironi, *Gazz. chim. ital.*, **47**, II, 6 (1917).

[6] Bevan, *Proc. Camb. Phil. Soc.*, **12**, 398 (1904).

[7] Bunsen and Roscoe, *Pogg. Ann.*, **100**, 43 (1857).

small fraction of the total amount of gas, the effect of the hydrogen added simultaneously was negligible.

The trap C was used to isolate the generator while measurements were being made. The capillary U-tube is constricted at one point so that a drop of solution can be held there by surface tension.[8] By immersing the trap in liquid air a plug of solid chlorine and ice is formed, which permits the reaction system to be pumped out, through J, without affecting the generator.

The photochemical reaction cell E is similar in design and size to that used by Porter, Bardwell and Lind.[1] The radiochemical reaction cell is a sphere 5.0 cm. in (inside) diameter, having an a-ray bulb mounted at its center. In order that it might be sealed to the apparatus the a-ray bulb was made of pyrex. This can be done quite readily by a technique differing only slightly from that described by Lind.[9] The bulbs were blown in a quartz furnace heated with a gas–oxygen flame, using compressed air (at approximately 6-lb. pressure) instead of a foot bellows.

Radon was introduced into the apparatus sealed in a thin capillary, which was placed through the "eye" in the top of the central steel rod in the breaking vessel L. The capillary was broken by revolving the rod, which extended through a hard rubber stuffing gland and a double mercury seal. After breaking the capillary the radon was condensed just below the reaction bulb by means of liquid air in a Ramsay liquid air funnel. The mercury was then brought just below the radon, before it was released by warming, to minimize absorption or trapping along the wall. The setting valve F is a modification of that described by Lind.[9]

The circulating pump was of the type described by Livingston,[10] and was capable of producing a rapid regular rate of flow.

The capillary used for the actinometer was selected for uniformity by measuring the length of a thread of mercury at different points along its length. It was calibrated by determining the length of a thread of mercury of known weight.

The quantity of radon used was determined by the gamma-ray method by comparison with a standard tube certified by the Bureau of Standards.

A 75-watt gas-filled tungsten lamp, situated one meter from the reaction cell was used as a secondary standard in the determination of the temperature coefficient of the radiochemical reaction. In the determination of the temperature coefficient of the photochemical reaction 75- and 200-watt lamps were used. They were run on 109 volts a. c., the voltage across the lamp being maintained by a hand regulated series resistance. In some of the experiments blackened copper gauzes were used to reduce the intensity of the light.

The monochromatic source, used as a radiation standard, consisted of a quartz mercury arc, equipped with the lenses and diaphragms necessary to produce a gradually converging pencil of light. The light beam passed through Corning filters *G585* and G38 and a crown glass absorption cell containing a 5% copper chloride solution. The emitted radiation was practically pure monochromatic light of 4358 Å. The arc was run at 52 volts and 3.0 amperes d. c. Variations in the line voltage and the room temperature were counterbalanced by an adjustable series resistance and forced ventilation of the lamp housing. The constancy of energy emitted was checked by direct measurement on several occasions during the course of the work.

The energy measurements were made with a Moll thermopile and a sensitive low-

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[8] Compare Ref. 1, p. 2607.

[9] Lind, "Chemical Effects of Alpha Particles and Electrons," Chemical Catalog Co., New York, 1928, pp. 86–88.

[10] Livingston, J. *Phys.* Chem., 33,955 (1929). The drawing in this article is printed upside down.

resistance Leeds and Northrup galvanometer. Deflections were observed on a ground glass scale placed one meter from the galvanometer. The system was calibrated by means of a radiation standard lamp furnished by the Bureau of Standards, for which the total radiation in absolute units at two meters distance in a given direction was known for various values of the current. When the calibrations were made a 15-ohm resistance was put in series with the galvanometer to reduce the deflection. Following the explicit directions furnished with the lamp, the results summarized in the following table were obtained.

TABLE I

CALIBRATION OF THE THERMOPILE AND GALVANOMETER

Amperes through filament[a]	Ergs mm.^{2} sec.[b]	Average deflection	Ergs/per mm. deflection mm.2 sec.
0.250	4.26	20.20	0.02109
.300	6.27	29.87	.02099
.350	8.67	41.00	.02115
		Av.	.02108 ± 0.00007

[a] The ammeter used in these measurements was kindly calibrated by Professor **A.** Zeleny of the Department of Physics. [b] Calibration of the Bureau of Standards for flux at *2* meters' distance from the lamp.

The deflections given in Column 4 are the averages of a large number of observations. The inside diameter of the thermopile horn is 2.60 cm. Assuming that all of the light falling in the horn is reflected onto the elements[11] the sensitivity of the system may be computed directly, as 0.02108 X (26.0/2) X π = 11.19 ergs/sec. per mm. deflection. Since the thermopile was equipped with a fluorite window, it is necessary to apply a correction for its absorption of the total radiation incident. If we take an approximate value for the transmission as 91%, the corrected value for the sensitivity is 10.18. Since the measurements of the energy of the monochromatic source were made with no extra resistance in the circuit, a correction must be applied for the 15 ohms used in calibration. A series of direct comparisons showed this factor to be equal to 0.677. The final value for the calibration is 6.89 ergs/sec. per mm. deflection.

The Temperature Coefficient of the Photochemical Reaction.—The apparatus used in the determination of the temperature coefficient of the photochemical reaction differed from that represented in Fig. 1 in that a second photochemical vessel (similar to the first) was introduced in place of the radiochemical vessel. These vessels were surrounded by separate thermostats, one of which was kept at room temperature, while the other was maintained at either room temperature or at 94°.

Reaction velocity measurements were made by illuminating alternately the first and second reaction vessels. In order to avoid the lag which follows a change in the intensity of activation, the method which Porter, Bardwell and Lind used for slow reactions[12] was not employed. The following method was adopted. Reaction Vessel I was illuminated, and the time required for the meniscus to move through a certain 50 cm. length

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[11] This was demonstrated for this instrument by B. Lewis, J. Phys. *Chem.*, 32, 278 (1928).

[12] Ref. 1, p. 2611.

of the actinometer capillary was determined; the illumination on Vessel I was shut off and Vessel II was illuminated; the meniscus was displaced by admitting more gas from the generator, and the time required for the meniscus to move through the 50 cm. length was taken. At least five such successive measurements were performed, and the average value of the ratio of the recorded times, with Vessel I and with Vessel II illuminated, was computed. The following typical computation will illustrate the method of taking the average.

TABLE II

COMPUTATION OF THE AVERAGE

A	B	C	D	E	
	201.5				
197.5		147		1.34	A/C
	193.5		140	1.38	A/D
189		133.5		1.42	A/C
	184.5		133	1.39	B/D
184		132		1.39	A/C
	183		131.5	1.39	B/D
		131			
			Av.	1.39	

Columns B and C give the times in seconds observed when Vessels I and II, respectively, were illuminated. Column A gives the averages between successive values in B, and Col. D gives the averages for C. As is indicated by the arrangement, values of B and C were determined alternately. Values of the ratio of the time required when Vessel I was illuminated are given in Column E. This term is equal to the ratio of the two reaction velocities, or, since the illumination was constant, to $(M/q)_{\mathrm{I}}/(M/q)_{\mathrm{II}}$, where M/q is the number of molecules reacting per quantum absorbed.

Rapid changes in sensitivity were never observed during the course of an experiment. A slow uniform drift in sensitivity was commonly observed (compare Table I), but did not appreciably affect the accuracy of the values of the ratio. We were unable to determine what factors were responsible for the sudden changes in sensitivity observed by Porter, Bardwell and Lind.[13] By the use of the two electrolytic generators the sensitivity could be controlled over a wide range. To increase the sensitivity the reaction system was first pumped out and then refilled by starting the hydrogen–chlorine generator (A). To reduce the sensitivity, the hydrogen–oxygen generator (B) was run for a few seconds.

To evaluate the temperature coefficient values of $(M/q)_{\mathrm{I}}/(M/q)_{\mathrm{II}}$ must be determined, first when both reactions occur at the same temperature, and second when one of them (I) occurs at a different temperature (94°). Since $(M/q)_{\mathrm{II},\,25^\circ}$ differs from $(M/q)_{\mathrm{I},\,25^\circ}$ only in the number of chains started per second (*i.e.*, by a constant factor), we may write

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[13] **Ref.** 1, p. 2611.

$$\frac{(M/q)_{94^\circ}}{(M/q)_{25^\circ}} = \frac{(M/q)_{\mathrm{I},\,94^\circ}}{(M/q)_{\mathrm{II},\,25^\circ}} \times \frac{(M/q)_{\mathrm{II},\,25^\circ}}{(M/q)_{\mathrm{I},\,25^\circ}}$$

The average variation of the reaction velocity per 10° interval over the range 25 to 98°, K_{10}, is given by the equation

$$\log K_{10} = \frac{10^\circ}{94 - 25^\circ} \log \frac{(M/q)_{94^\circ}}{(M/q)_{25^\circ}}$$

In computing values of K_{10} the measured room temperature, which varied from 21 to 27°, was used instead of 25°. A few measurements, Numbers 20 to 22, Table III, were made at 52°. The differences between the temperatures of the two thermostats (ΔT) is given in Col. 5. The values of $(M/q)_{94^\circ}/(M/q)_{25^\circ}$ listed are each based upon a series of measurements similar to that quoted in Table II. Only those series which showed a uniform drift in sensitivity, not greater than 6% between successive measurements, are recorded. The values of $(M/q)_{\mathrm{I},\,25^\circ}/(M/q)_{\mathrm{II},\,25^\circ}$ used in computing $(M/q)_{94^\circ}/(M/q)_{25^\circ}$ are each the average of from six to ten series of measurements.

In order to obtain an absolute value for the chain length, M/q, at which the temperature coefficient measurements were performed, a cylindrical absorption cell was sealed into the apparatus in place of one of the reaction vessels. The cell is 16.0 cm. long and has plane sealed-on ends 3.0-mm. thick. The monochromatic source was adjusted to throw a narrow pencil of light which passed through the cell and converged into the horn of the thermopile. Measurements were made of the energy passing through the cell when it was evacuated to less than a mm. pressure and when the reaction mixture circulated through it at one atmosphere pressure. The galvanometer deflection corresponding to the absorption by the gas was 3.20 cm. This corresponds to a rate of absorption of 6.89 ergs./sec. mm. × 32.0 mm. = 220.5 ergs./sec. This value must be corrected for the absorption by the second pyrex plate of the cell. Direct measurements with this plate, and measurements with 11.7 mm. of pyrex, gave a value for the transmission of the plate of 91%.[14] The absorption of the fluorite window for light of this wave length is practically negligible. Correcting for the absorption by the pyrex, the amount of energy absorbed is 243 ergs./sec. The energy per quantum is

$$E = \frac{6.56 \times 10^{-27} \times 3 \times 10^{10}}{4.36 \times 10^{-8}} = 4.51 \times 10^{12}\ \text{ergs. per quantum}$$

Therefore, the rate of absorption of quanta is $2.43 \times 10^2/4.51 \times 10^{-12} = 5.40 \times 10^{13}$ quanta per second.

By comparing the reaction velocity due to the monochromatic source with the velocities due to the white light sources used, the number of

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[14] This corresponds to a considerably lower value for the coefficient of absorption than that based on measurements of the transmission of a plate 0.77 mm., made by Gibson and McNichols in 1919, Bureau of Standards., Technical Paper 119 (1919).

quanta absorbed by the chlorine from the latter may be computed. *Since quanta of different frequencies are not equally effective in starting reaction chains,*[2] *the number of the quanta determined in this way is not equal to the actual number of quanta absorbed from the white light, but rather to the number of quanta of λ4358 Å. which would be required to maintain the same rate.* The values of M, used in computing M/q, were obtained from the calibration of the actinometer capillary; 1.00 cm. displacement corresponds to 0.0504 cc. By combining this factor with Avogadro's number and the observed rate of displacement of the meniscus (in cm. per sec.), M, the number of molecules reacting per second can be obtained. The detailed results of the comparison of the monochromatic source with the 75-watt lamp are given in Table III.

TABLE III

COMPARISON OF A 75-WATT LAMP WITH THE MONOCHROMATIC SOURCE

$(M/q)_w/(M/q)_{4358}$	0.174	0.185	0.159	0.152	0.173	0.172	
$q \times 10^{-13}$, 4358 Å.	5.40	5.40	5.40	5.40	5.40	5.40	
$q \times 10^{-13}$, white	0.94	1.00	0.86	0.82	0.94	0.93	Av. 0.92 ± 0.05
$M/q \times 10^{-13}$	16	18	23	39	43	49	

The other white light sources were compared to the 75-watt lamp in a similar manner. The number of quanta absorbed per second for each of these is indicated in Col. 3 of Table IV.

TABLE IV

TEMPERATURE COEFFICIENT OF THE PHOTOCHEMICAL REACTION

Number	$q \times 10^{-13}$	$(M/q)_{94°}/(M/q)_{25°}$ Obs.	Corr.	AT°	$M/q \times 10^{-3}$	K_{10}
1	2.45	2.09	2.26	69	5.1	1.124
2	2.45	2.25	2.43	70	5.8	1.134
3	2.45	1.99	2.05	70	6.1	1.115
4	2.45	2.03	2.19	65	7.4	1.126
5	2.45	2.14	2.31	68	7.4	1.128
6	2.45	2.12	2.29	69	8.6	1.126
7	2.45	2.00	2.16	71	9.4	1.122
8	2.45	2.03	2.19	69	15.5	1.119
9	2.45	1.84	1.99	68	16	1.105
10	2.45	1.95	2.11	68	16.5	1.114
11	2.45	1.88	2.03	67	19	1.109
12	2.45	1.82	1.97	67	19.5	1.104
13	0.92	2.58	2.79	67	20	1.163
14	.92	2.67	2.88	67	22	1.169
15	.92	2.66	2.87	68	23	1.166
16	.92	2.69	2.91	68	28	1.168
17	.92	2.71	2.93	68	28	1.169
18	.256	3.12	3.37	67	33	1.204
19	.256	3.26	3.62	69	46	1.206
20	.256	1.69	1.74	28	66	1.217
21	,256	1.64	1.69	28	66	1.205

TABLE IV *(Concluded)*

Number	$q \times 10^{-13}$	$(M/q)_{94^\circ}/(M/q)_{25^\circ}$ Obs.	Corr.	AT^0	$M/q \times 10^{-3}$	K_{10}
22	0.256	1 67	1 72	28	69	1.213
23	.256	3 76	4 06	67	69	1.224
24	.256	3.47	3.75	68	79	1.219
25	.256	3.35	3 62	69	81	1.210
26	.256	3.71	4 01	68	92	1.230
27	.167	4 33	4 68	72	119	1.238
28	.167	4 10	4 43	71	119	1.231
29	.167	2 78	3 00	68	130	1.174
30	.167	2 57	2.78	67	152	1.164
31	.167	2 55	2 75	67	158	1.162
32	.167	2.93	3 16	67	170	1.186

In Fig. 2 the values of K_{10} are plotted (as black dots) against the average chain length, M/q. As may be readily seen from this plot, the value of K_{10} depends on the sensitivity, or average chain length. It is least for low sensitivities and rises to a constant value or flat maximum for M/q equal to 10^5.

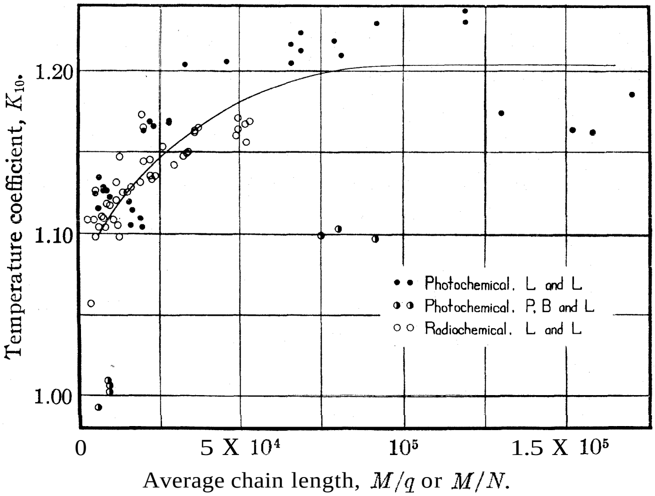

Fig. 2.—The temperature coefficient.

Since it proved difficult to attain the highest sensitivities, comparatively few measurements were made for chain lengths greater than 10^5, and it is possible that the values of K_{10} corresponding to the highest sensitivities are less accurate than those in the intermediate range. It should be noted that these values are not in agreement with those published by Porter, Bardwell and Lind[1] (which are indicated by half-blackened circles in Fig. 2), although both sets of data show the same trend with sensitivity. The explanation of this discrepancy is not known.

It should be of interest to compare the values of the temperature coefficient given here with those published by other investigators.[1,5,6] Since these measurements were made for different temperature intervals, probably the simplest way of comparing them is to plot the logarithm of the reaction velocity against the absolute temperature. Such a plot is given in Fig. **3**. Arbitrary quantities have been added to each of the several series of values of log v such that they coincide at T = 29S°K. The values taken from Table IV are the average of Numbers 20, 21 and 22 for 52°, and Number 23 for 94°; these values correspond to an average chain length of about 68,000. All of the values plotted represent experiments with white light. The values taken from the work of Porter, Bardwel and Lind correspond to a chain length of about 80,000. Except for the values of Porter, Bardwell and Lind, all of the results are in as good agreement as could be expected, particularly when it is remembered that the sensitivity of the mixtures used by Bevan[6] and by Padoa and Butironi[5] are not known. The data also indicate that the Arrhenius equation holds at least approximately for this reaction. In view of the complex nature of the reaction, this latter result is rather surprising.

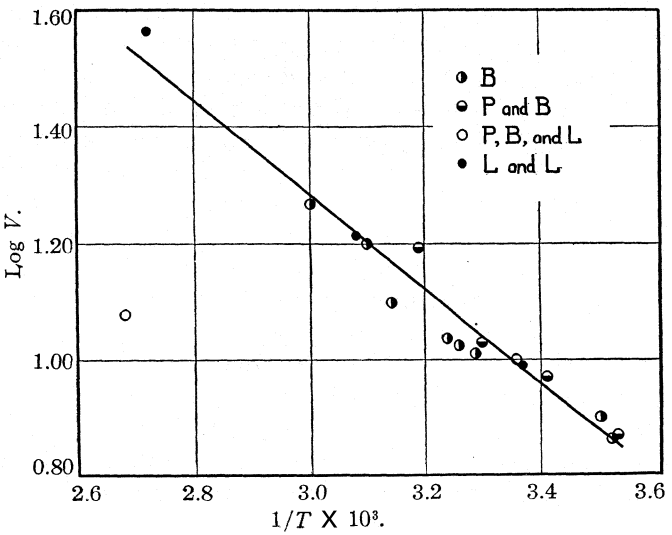

Fig. 3.—Comparison of rate measurements at different temperatures.

The results of Padoa and Butironi[6] indicate that the value of K_{10} is greatly affected by the wave length of the absorbed light. To test this result a few measurements were made with a 100-watt light and a 5-cm. filter of saturated nickel sulfate solution. The values of the temperature coefficient so obtained were unmistakably larger; about 1.29 for $M/q = 10^5$. However, this is much smaller than the value of 1.5 obtained by

Padoa and Rutironi. The results of these latter experimenters may be influenced by their experimental conditions. If their reaction was preceded by an induction period of measurable length, then reducing the number of effective quanta absorbed per second, as in going to light of longer wave length by means of filters, would very probably produce an apparent increase in the temperature coefficient. In a recent preliminary report, Allmand and Beesley[2] state that "experiments carried out at 19.7 and 25° showed the relative temperature coefficients of the quantum efficiency to increase slowly, but unmistakably, with λ between 313 and 436mμ."

In view of the fact that Franck[15] has shown that chlorine dissociates into an excited and a normal atom as a primary act on absorption of a quantum of frequency greater than the convergence frequency of chlorine (which corresponds to λ4785 Å.), it is difficult to explain the results of Allmand and Beesley.[2] However, if a quantum of light, of wave length greater than 4785 Å. but still containing nearly enough energy to dissociate a chlorine molecule, is absorbed, it is quite probable that the resulting activated molecule can be dissociated by means of a collision.[16] It is very probable that activation of this type does possess a relatively large temperature coefficient.[17] This fact may be responsible for the higher temperature coefficient observed when "green" light (or monochromatic light of 5460 Å.) is used; but it does not explain Allmand and Beesley's result for shorter wave lengths. Since they determined the amount of absorption by measuring the incident intensity and computing the absorption from von Halban and Siedentopf's data,[18] it is possible that the explanation of their results lies in the effect of temperature on the absorption coefficient of chlorine for the several frequencies used.[19]

Temperature Coefficient of the Radiochemical Reaction.—The methods used in determining the temperature coefficient of the radiochemical reaction were similar to those used in the study of the photochemical reaction. The apparatus is represented in Fig. 1. The thermostat surrounding the photochemical vessel was kept at room temperature or at 98°.

Reaction velocity measurements were made alternately, when the activation was due to a-rays alone, and when it was due to both a-rays

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[15] Franck, Trans. *Faraday Soc.*, *21*, 536 (1925).

[16] Compare Kistiakowsky, "Photochemical Processes," Chemical Catalog Co., Inc., New York, 1928, p. 98.

[17] Compare, however, the results of Jost [*Z. physik. Chem.*, 134, *92* (1928)], who found no difference in the efficiency of light from either side of the bromine convergence in producing the synthesis of hydrobromic acid.

[18] Von Halban and Siedentopf, *ibid.*, 103, 80 (1923).

[19] The effect of this phenomenon on the observed values of the temperature coefficient of photochemical reactions has been discussed by Kistiakowsky, Ref. 16, pp. 248–251.

and light. The experimental procedure and the method of averaging have been described in connection with the photochemical reaction. In this case, however, the average so obtained is the ratio of the sum of the two reaction velocities to that of the radiochemical reaction. In order to reduce a series of such values to a common basis, it is necessary to correct for the decay of radon.

$$e^{-\lambda t}\left(\frac{v_q + v_\alpha}{v_\alpha} - 1\right) = e^{-\lambda t}\,\frac{v_q}{v_\alpha} = \frac{(M/q)_{25^\circ}}{(M/N)_+}$$

Since the work of Porter, Bardwell and Lind demonstrates that the ratio $(M/N)/(M/q)$ is not dependent on sensitivity, these values may be used to obtain $(M/N)_{98^\circ}/(M/N)_{25^\circ}$ by the method already described. The values so computed are not an exact measure of the temperature coefficient, since the total ionization is not independent of the temperature. The ionization is proportional to the density of the gas or inversely proportional to the absolute temperature. Therefore

$$\frac{371^\circ}{298^\circ} \times \frac{(M/N)_{98^\circ}}{(M/N)_{25^\circ}\text{ obs.}} = \frac{(M/N)_{98^\circ}}{(M/N)_{25^\circ}\text{ corr.}}$$

The corrected values were used in computing K_{10}.

To determine the number of ion pairs formed per second per millicurie with the a-ray bulb and reaction sphere used, the sphere was sealed into a manometric system, 182.3 millicuries of radon was placed in the bulb, and the reaction system was filled with a stoichiometric mixture of hydrogen and oxygen at atmospheric pressure. The pressure change was followed for five days, and kE_0/λ was determined, by plotting $\log P_{H_2 + O_2}$ against $e^{-\lambda t}$, to be equal to 0.723. This corresponds to 3.23×10^{15} ion pairs per second per millicurie, in a stoichiometric mixture at N. T. P. If it is assumed that the total ionization in the sphere is proportional to the specific ionization of the gas,[20] it follows that the number of ion pairs formed per second per millicurie in an equimolar hydrogen–chlorine mixture is $(1.33/0.527)10^{-3} \times 3.23 \times 10^{15} = 8.15 \times 10^{12}$. At 22° and 740-mm. pressure (average values for the room temperature measurements) the corresponding value is 7.35×10^{12}. The method of computing M has already been outlined. The values of $(M/N)_{98^\circ}$ were corrected to 25° by dividing by the corresponding values of $(M/N)_{98^\circ}/(M/N)_{25^\circ}$.

A plot of K_{10} against $(M/N)_{25^\circ}$ is included in Fig. 2, the experiments being represented as circles. As in the case of the photochemical reaction, the temperature coefficient is a function of the sensitivity.

The Relative Efficiency of Photons and Ions.—The experimental data,

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[20] This assumption is not in general justifiable. However, Porter, Bardwell and Lind[1] point out that the work of Bardwell and Doerner [THIS JOURNAL, *45*, *2593 (1923)*] shows that for spheres of less than 3 cm. radius the intensity of ionization is very nearly constant along this path. Therefore, although the method of calibration used here is not exact, the results are probably not in error by more than *10%*.

TABLE V

TEMPERATURE COEFFICIENT OF THE RADIOCHEMICAL REACTION

No.	Millicuries of radon	$\frac{(M/N)_{98°}}{(M/N)_{25°}}$ Obs.	$\frac{(M/N)_{98°}}{(M/N)_{25°}}$ Corr.	$\frac{(M)}{(N)} \times 10^{-3}$	K_{10}
1	3.98	1.20	1.49	3.5	1.057
2	3.92	1.67	2.08	2.5	1.108
3	2.91	1.73	2.15	9.5	1.117
4	2.90	1.85	2.30	16	1.128
5	2.44	1.81	2.25	8.5	1.118
6	2.03	2.08	2.58	11.5	1.120
7	2.02	2.18	2.72	12.5	1.147
8	1.45	1.65	2.06	12	1.105
9	1.44	1.58	1.97	12.5	1.098
10	1.41	2.08	2.58	20	1.144
11	1.40	1.93	2.40	19	1.131
12	2.86	2.04	2.54	11.5	1.131
13	2.40	1.93	2.40	13.5	1.125
14	2.22	1.69	2.10	8	1.104
15	2.22	1.75	2.18	7.5	1.109
16	1.93	1.98	2.46	15	1.125
17	1.92	2.28	2.84	22	1.145
18	1.92	2.13	2.65	23.5	1.135
19	1.56	2.08	2.59	22.5	1.133
20	1.55	2.11	2.62	22	1.135
21	1.38	2.20	2.74	29.5	1.142
22	1.38	2.37	2.95	26	1.153
23	1.17	2.52	3.13	36	1.162
24	1.16	2.43	3.03	52	1.156
25	0.94	2.59	3.22	19.5	1.173
26	.94	2.46	3.06	20	1.165
27	.75	2.26	2.81	33.5	1.149
28	.75	2.24	2.79	32.5	1.147
29	.74	2.28	2.84	34	1.150
30	.63	2.62	3.21	49.5	1.171
31	.63	2.50	3.11	49.5	1.164
32	.63	2.44	3.04	49	1.160
33	.55	2.65	3.33	37	1.165
34	.55	2.44	3.04	36	1.163
35	.54	2.68	3.34	53	1.169
36	.54	2.64	3.28	51.5	1.167
37	3.58	1.75	2.18	10.5	1.108
38	3.55	1.79	2.22	7	1.110
39	3.53	1.71	2.13	6	1.104
40	3.51	1.98	2.46	5	1.126
41	3.02	1.75	2.18	4.5	1.108
42	2.96	1.64	2.04	5	1.098

summarized in Tables IV and V, demonstrate that the value of the temperature coefficient of the reaction rate is practically the same for the photo- and radiochemical reactions. This, as well as the fact that the temperature coefficient is a function of sensitivity, indicates that the temperature coefficient is determined by the secondary or chain mechanism[21] and that this mechanism is independent of the form of activation. Additional evidence for this latter point has been presented by Porter, Bardwell and Lind,[1] who have demonstrated that the ratio of the yield per ion pair to the yield per absorbed quantum is independent of the sensitivity of the mixture. For measurements at 25° they find the value of this ratio to be 3.72. They assume that K_{10} for the radiochemical reaction is equal to unity and therefore that the ratio is a function of temperature, probably equal to 2.0 at 100°. However, the measurements of the temperature coefficient presented here indicate that the ratio is independent of the temperature, at least for the range 25 to 100°.

In the determination of the radiochemical temperature coefficient, a number of values of $(M/N)_{25°}/(M/q)_{25°}$, in arbitrary units, were determined. By introducing the number of ion pairs produced per second and the number of quanta absorbed per second (Table III) this ratio may be converted into absolute units.

$$\frac{(M/N)_{25°}}{(M/q)_{25°}}\ \text{absolute} = \frac{q}{E_t \times 7.35 \times 10^{12}} \times \frac{(M/N)_{25°}}{(M/q)_{25°}}\ \text{arbitrary}$$

where 7.35 × 10^{12} is the number of ion pairs per second per millicurie. The average value of $(M/N)/[E_+ \times (M/q)]_{\text{arbitrary}}$ for three series of measurements (involving three separate charges of radon in the same bulb, 27 determinations in all) is 1.36 ± 0.21. The corresponding value of $(M/N)_{25°}/(M/q)_{25°\,\text{absolute}}$ is 0.92. Since this determination involves an indirect measure of the number of quanta absorbed, as well as possible uncertainties in the quantity of radon, the measurement was repeated under more definite conditions.

A new radiochemical vessel was calibrated by means of the hydrogen–oxygen reaction, and was found to give 9.45 × 10^{12} ion pair per millicurie for an equimolar mixture of hydrogen and chlorine at 740 mm. and 22°. Without removing the charge of radon this vessel was sealed into a circulating system containing the light absorption cell. The radon was allowed to decay to about 7 millicuries. It has already been shown that under the experimental conditions employed 5.40 X 10^{13} quanta per second of λ4358 were absorbed by the chlorine. Using a reaction mixture of low sensitivity (M/N about 4000), three series of measurements of $(M/N)/(M/q)$ were made. Two days later, when an attempt was made to repeat the measurements using a more sensitive mixture an explosion ensued which wrecked the entire apparatus. The average value of $(M/N)_{25°}/(M/q)_{25°}$ abs. based upon the three experiments is 1.18. This is in good agreement with the value obtained by the indirect comparison, but is about three-fold smaller than that published by Porter, Bardwell and Lind.

Very recently Allmand and Beesley[2a] have published a preliminary

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[21] Compare Cremer, Ref. 3.

notice of work which indicates that quanta of different wave lengths differ materially in their chemical efficiency. They state that the efficiency curve has a maximum at 4050 Å. If the factor for 4050 Å. is taken as unity, the value for 4358 Å. is 0.67. Therefore, if monochromatic light of 4050 Å. instead of 4358 Å. had been used in these experiments, the values for $(M/N)/(M/q)_{\text{abs}}$. would have been $0.92 \text{ X } 0.67 = 0.62$ and $1.18 \times 0.67 = 0.79$, within the limits of experimental error still equal to unity. A similar correction must be applied to Porter, Bardwell and Lind's value of 3.72. However, there are apparently two errors in the computation of this value which should be corrected for first. The total number of ion pairs per a-particle should be $2.47 \times 3.72 \times 10^4 = 9.19 \times 10^4$ not $8.45 \text{ X } 10^4$.[22] Correcting this to 25°

$$9.19 \text{ X } 10^4 \text{ X } 273/298 = 8.41 \times 10^4 \text{ ion pairs per particle.}$$

This corresponds to $1.003 \times 10^{18} \times 8.41 \times 10^4 = 8.44 \times 10^{12}$ ion pairs/sec. per millicurie, for the total ionization in the bulb. Repeating their graphical determination of the mean wave length of the light absorbed by the chlorine results in a value of 4350 Å., not 4100 Å. as published. In this computation we have used Priest's[23] values for the energy distribution from a 500-watt tungsten lamp.

There appears to be considerable uncertainty in the published values for the extinction coefficient for copper sulfate solution. The values used were graphical averages of the data of Martens and Grunbaum[24] for 0.62 M solution, of van der Gon[25] for 1.15 M solutions, and of Mecke and Ley[26] for 0.50 M solutions. The method of taking the average (particularly in the region 3600 to 5000 Å.) has a large effect on the values for the average wave length of the light absorbed by the reaction mixture, and a still greater effect on the average efficiency term (Allmand's factor). It is apparently one of the chief sources of uncertainty in the corrected value for $(M/N)/(M/q)$ based upon the work of Porter, Bardwell and Lind.[1] No correction was made for the absorption of crown glass, partly because it is practically independent of the wave length for the region 4000 to 6000 Å. and partly because the thickness of the glass in the optical path is not given. The absorption of chlorine is taken from the work of von Halban and Siedentopf.[18]

From these data a curve of the energy absorbed (in arbitrary units) against wave length was plotted. The corresponding curve of relative

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[22] Ref. 1, p. 2609.

[23] Priest, J. Opt. *Soc. Am.*, *6*, 27 (1922). The filament (color) temperature of this 500-watt lamp was 2848°, not 2700°K. as used by Porter, Bardwell and Lind. However, if 2700° were used it would result in an even greater value than 4350 Å. for the mean wave length.

[24] Martens and Grunbaum, *Am.* **Physik,** 12,1004 *(1903).*

[25] Van der Gon, *Arch. ne'erl,* 7, *140* (1923).

[26] Mecke and Ley, *Z. physik. Chem* , 111,385 (1924)

number of quanta absorbed against wave length was plotted, and a mean value (4350 Å.) which divided the area under the curve into two equal parts was determined. The corrected value for $(M/N)/(M/q)$ is

$$3.72 \times \frac{4350}{4100} \times \frac{7.84 \times 10^{12}}{8.44 \times 10^{12}} = 3.67$$

Using Allmand and Beesley's[2a] table of efficiency factors and the plot of relative number of quanta absorbed, a curve of relative number of "effective quanta" was plotted against wave length. The ratio of the total areas under these two curves is the efficiency factor (in terms of λ4050 Å.). Using this factor (0.71), Porter, Bardwell and Lind's value of $(M/N)/(M/q)$ reduces to 0.71 X 3.67 = 2.6.

The average of these three values for $(M/N)/(M/q)$ is 1.3. Although the close agreement between this value and unity is apparently fortuitous, it is fairly certain that the correct value is not greater than 2.0, and is quite probably unity.

The Mechanism of the Reaction.—While the results presented here indicate that the chain mechanism is independent of the form of activation, they do not offer any direct evidence in regard to the nature of that mechanism. However, it is possible to draw certain conclusions about the mechanism of activation. It is now generally accepted that photochemical activation, by light of wave length less than 4785 Å., can be represented as

$$h\nu + Cl_2 = Cl + Cl'$$

A possible corresponding mechanism for the activation by α-rays is

$$Cl_2^+ + (-) = Cl + Cl' \text{ or } Cl_2^+ + Cl_2^- = Cl_2 + Cl + Cl' \text{ or } Cl_2 + (a) = Cl + Cl^+ + (-)$$

These two equations would indicate a value of unity for the ratio $(M/N)/(M/q)$. If the correct value for this ratio were 2.0, a corresponding activation involving negative molecular ions could be assumed

$$Cl_2^+ + Cl_2^- = 2Cl + 2Cl'$$

Of course, both of these processes might occur simultaneously. The experimental evidence seems to indicate that the latter process occurs less frequently than the former.

There is an apparent inconsistency between the results presented here and by Porter, Bardwell and Lind,[1] which show that an ion is very effective in starting a chain, and the results of Allmand and Beesley,[2a] which show that a quantum of *ultraviolet* light is a relatively inefficient source of activation.

Summary

1. The photochemical (white light) and radiochemical synthesis of hydrogen chloride have temperature coefficients which are identical within the limits of experimental error.

2. The temperature coefficient of this reaction varies with the sensitivity of the reacting mixture. The 10° coefficient has a value of about

1.10 for an average chain length of 2×10^3, and rises to a constant value, or flat maximum, of about 1.20 for an average chain length of 8×10^4.

3. It has been shown qualitatively that the temperature coefficient has a value about 10% higher when "green light" (a $NiSO_4$ filter) is used as the source of activation.

4. An absolute value, of approximately *unity,* for the ratio of the yield per ion pair to the yield per absorbed quantum was obtained using monochromatic light of λ4358 Å. The results of Porter, Bardwell and Lind[1] are discussed, and a correction based upon the work of Allmand and Beesley[4] has been applied.

5. **A** mechanism of activation, consistent with the results presented here, is outlined.

MINNEAPOLIS, MINNESOTA

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

THE OXIDATION OF IODIDE ION BY PERSULPATE ION. III. THE IODIMETRIC ESTIMATION OF PERSULFATES

BY CECIL V. KING AND ERIC JETTE

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In the second paper of this series the velocity of the reaction between persulfate and iodide ions in alkaline solutions was reported. The iodine produced disappears almost as fast as formed, producing iodate and iodide (through the intermediate formation of hypoiodite); the liberation of iodine on acidifying was assumed to be quantitative. Some of our experiments suggested that the amount of iodine recovered was slightly low. Consequently the iodimetric estimation of persulfate in neutral and alkaline solutions was carefully compared.

A number of previous investigations have proved that persulfate liberates iodine from potassium iodide with quantitative precision in neutral solution[1] and we have fully confirmed this. The reaction is slow, but can be hastened enormously by inert salts, special catalysts, etc., as shown in the papers mentioned.

Experimental

(1) Liberation of Iodine in Neutral Solution.—We first compared the amount of iodine liberated by potassium permanganate in acid solution with that liberated by an equivalent amount of potassium persulfate in neutral solution. The permanganate was carefully standardized, and the concentrations and conditions used in liberating iodine were well

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[1] See Miiller and Ferber, Z. anal. *Chem.,* 52, 195 (1913); Muller, *ibid.,* 52, 299 (1913); Schwicker, *ibid.,* 74, 433 (1928); Zombory, *ibid.,* 73, 217 *(1928).* References to other literature will be found in these papers.

within the limits recommended by Bray and Miller, who have concluded that the permanganate method for standardizing thiosulfate solution is accurate to one part per thousand.[2] Potassium persulfate was recrystallized three times between 50 and 0° and dried over sulfuric acid. Standard solutions were made by weighing out the crystals; 0.008 and 0.04 M solutions of persulfate were used. Samples of these solutions, potassium iodide and potassium chloride (to hasten the reaction) were sealed in glass bulbs (to avoid loss of iodine by volatilization) and allowed to stand for one to three hours. Several series of experiments showed agreement to one part per thousand between the two methods. For example, using 0.008908 *M* permanganate ($\pm 0.03\%$) a thiosulfate solution was 0.009841 *M* ($\pm 0.04\%$); using 0.008 *M* persulfate to liberate the iodine, the thiosulfate was 0.009847 *M* ($\pm 0.05\%$). Other trials gave equally good agreement.

(2) The Reaction in Alkaline **Solution.**—Müller and also Schwicker[1] have claimed quantitative results when iodine is liberated by persulfate in alkaline solution which is later acidified just before titration. Most of Müller's titrations show 1 to 2 parts per thousand less iodine than the theoretical, but it is hard to tell from Müller's paper whether this is significant or not. Schwicker reports most of his titrations only to 0.1 cc. and consequently his degree of precision is doubtful. We feel that our experiments are comparable in accuracy to those of Bray and Miller[2] on the use of permanganate in standardizing thiosulfate solutions.

Our very carefully made comparisons show that the iodine liberated in alkaline solution is invariably 2 to 5 parts per thousand lower than the amount which is liberated in neutral solution. The following example from a series of twenty comparisons made will illustrate: neutral solution, 25 cc. of 0.008 M persulfate + 5 cc. of M KI + 4 g. of KCl required 40.11, 40.14, 40.13, 40.12 cc. of thiosulfate solution; alkaline solution, 25 cc. of 0.008 M persulfate + 5 cc. of M KI + 10 cc. of M NaOH (from sodium), acidified later, required 40.03, 40.04, 40.02, 40.03 cc. of the same thiosulfate solution. In all other experiments, with persulfate 0.008 M and 0.04 M, the results were similarly low. The difference is quite outside experimental error. We recommend that if the alkaline solution method is used, the results be increased by three parts per thousand to be in agreement with the very accurate neutral solution method.

(3) Investigation of this Inaccuracy.—It has apparently been taken for granted that when iodine solution is made alkaline and then acidified, the iodine is quantitatively recovered. However, we have found that this is not the case. In a series of comparisons it was found that the iodine recovered was almost invariably 2 to 5 parts per thousand lower than that in the same sample titrated directly with thiosulfate. For example:

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[2] Bray and Miller, This Journal, 46, 2204 (1924).

25 cc. of 0.00880 *M* iodine (in 0.1 *M* KI) titrated directly required 20.57, 20.59, 20.55, 20.60 cc. of thiosulfate. The same sample + 5 cc. of 3 N sulfuric acid required 20.60 and 20.58 cc. of thiosulfate. The same sample run into 20 cc. of 3 M NaOH (from sodium), immediately acidified, required 20.52, 20.53 and 20.53 cc. of thiosulfate; acidified after standing for one hour, 20.49 and 20.50 cc. of thiosulfate. About fifty other samples run at widely different times, with different lots of materials, with iodine from 0.005 to 0.02 M and NaOH from 0.5 to 1.5 M, gave results 2 to 5 parts per thousand low in the alkaline solutions.

We are sure that these results are not due to experimental error. All precautions were taken to avoid loss of iodine by volatilization. Sodium hydroxide which had been purified by alcohol was avoided (see Müller, Ref. 1). Comparisons were made under exactly similar conditions. The inaccuracy of the liberation of iodine by persulfate in alkaline solution is undoubtedly due to the same cause as the loss of iodine when the solution is made alkaline and then acid.

The only reasonable explanation seems to be that hypoiodous acid or hypoiodite ion decomposes in some manner such that part of the iodine does not reappear on acidifying. Hypoiodous acid, being more of a base than an acid, exists to an appreciable extent in alkaline solution; it may decompose as follows

$$2HIO \longrightarrow 2I^- + 2H^+ + O_2\text{, or perhaps } 2IO^- \longrightarrow 2I^- + O_2$$

The yellow color (which does not disappear immediately on making the solution alkaline) and the odor presumably indicate the presence of hypoiodous acid in the alkaline solution.

Summary

1. The amount of iodine liberated from potassium iodide by persulfate in neutral solution is shown to agree within one part per thousand with that liberated by an equivalent amount of permanganate in acid solution. Persulfate is therefore recommended as an oxidimetric standard in iodimetry.
2. When the liberation is carried out in alkaline solution which is acidified just before titration, the results are 2 to 5 parts per thousand low; no way has been found to eliminate this error.
3. When a solution of iodine in potassium iodide is made alkaline, then acidified, 2 to 5 parts per thousand of the iodine are lost. This probably explains conclusion (2).

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE]

THE HEAT CAPACITY OF SATURATED LIQUID ETHANE FROM THE BOILING POINT TO THE CRITICAL TEMPERATURE AND HEAT OF FUSION OF THE SOLID[1]

BY R. WIEBE,[2] K. H. HUBBARD[3] AND M. J. BREVOORT[4]

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The data presented in this paper are the results of further work on a series of investigations that are being carried out on the properties of ethane.[5] Measurements on the heat capacity of saturated liquid ethane have recently been made by A. Eucken and F. Hauck,[6] but their results are 10 and in some instances even 20% higher than ours; we shall discuss the relative merits of the data later.

The purpose of this investigation is to gain additional knowledge of the thermal properties of one of the constituents of natural gas from which helium is being extracted.

Preparation of Ethane.—The preparation of large quantities of pure ethane was difficult. At low temperatures 2.3 moles were necessary to fill the calorimeter, and altogether more than 12 moles of the substance were made.

Ethane was generated by electrolyzing a solution of potassium acetate as outlined by Murray.[7] The gas was passed successively and repeatedly through 30% solution of sodium hydroxide, fuming sulfuric acid, concentrated sulfuric acid, 30% solution of sodium hydroxide, potassium hydroxide sticks and phosphorus pentoxide. The liquefied gas was finally fractionated twice under stirring in a cryostat; the first and last portions were rejected. Before the final fractionation, several portions had been rejected during the process of chemical purification. From the heat effect associated with premelting and lowering of the melting point, the purity was estimated to be about 99 mole per cent. Two batches of ethane were initially prepared. The second batch showed signs of only slightly higher purity than the first one, even though considerably more care was used in its preparation. The fillings for the steel calorimeter were taken from the second batch and should have been of progressively greater purity as the amount of ethane in the calorimeter decreased.

Apparatus.—The apparatus for temperature control, similar to that used by Gibson and Giauque[8] is shown in Fig. 1.

The copper cylinder, B, weighing 3.8 kg., was suspended from the steel top of a vacuum-tight container, A, made from a solid brass cylinder. A lead gasket, D, was

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[5] Loomis and Walters, THIS JOURNAL, 48, 2051 (1926); Frank Porter, *ibid.*, 48, 2055 (1926).

[6] A. Eucken and F. Hauck, Z. *physik.* Chem., 134,161 (1928).

[7] Murray, J. Chem. *Soc.*, 61, 10 (1892).

[8] G. E. Gibson and W. F. Giauque, THIS JOURNAL, 45, 93 (1923).

found quite satisfactory even at liquid–air temperatures, although it was necessary to tighten the nuts on the stud screws occasionally. The pressure was ordinarily less than 3×10^{-5} mm. of mercury. H and J were heating elements connected in series. The heater, J, was added to the apparatus after it was found that the temperature of the top lagged considerably behind the temperature of the body of the copper cylinder because of poor contact. One of the thermometer terminals is shown at G; F is a bakelite tube for thermocouple leads. The Wood's metal seal, E, insured good thermal contact with the steel tube leading to the calorimeter. The places marked TC indicated the positions of different thermocouples.

Two calorimeters as shown in Fig. 1 were used, a steel calorimeter, C, primarily for pressures above 1 atmosphere, and one made of copper, P, for low pressures.

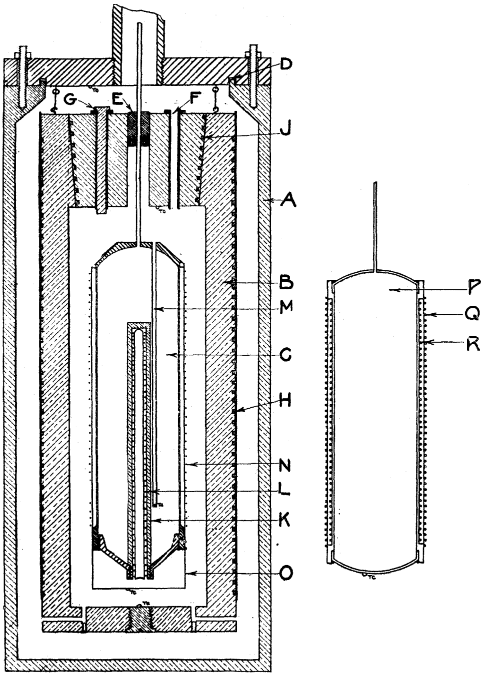

Fig. 1.—Apparatus for specific heat measurements.

The cylindrical steel calorimeter, C, had a wall thickness of 1.0 mm. The height was 14 cm., the diameter 3.8 cm. and the volume 123.3 cc. The bottom steel cap was screwed into the body of the calorimeter and the joint was made pressure tight by silver-soldering in a groove left for that purpose. A central heater tube, K, 10 cm. in length, made of a solid copper cylinder with twelve radial vanes cut out in a milling machine, was screwed and silver-soldered into the bottom cap. The heater, L, was wound around a thin copper tube closed on one end and in thermal contact with the central heater tube by means of Rose metal. A thermocouple well, M, of copper was extended from the top.

The steel calorimeter, C, was surrounded by a copper shell, O, 1.5 mm. thick, in order to equalize rapidly the outside temperature. The copper resistance thermometer, N, was wound on this copper sheet. The latter made contact only at the top and bottom of the cylindrical portion, which eliminated any strain in the thermometer due to differential expansion.

The copper calorimeter, P, had a wall thickness of 0.75 mm. The height was 13 cm. and the diameter 3.8 cm. Sixteen radial vanes of copper served to distribute the heat rapidly throughout the calorimeter. Ethane was introduced through a steel tube (O.D. 0.25 cm. and I.D. 0.19 cm.). Resistance thermometer Q and heater R were separate. The former was made of No. 40 B. and S. gage copper wire and had a resistance of 240 ohms at 0°. The resistance thermometer was wound on the outer shell which was soldered to the calorimeter, while the heater, made of No. 32 B. and S. gage manganin wire, was wound around the body of the calorimeter. The resistance of the heater was 620 ohms at room temperature and remained very constant because of the small temperature coefficient of manganin wire. In using a copper resistance thermometer we followed Onnes and Holst,[9] Meissner[10] and others. The volume of the copper calorimeter was 144.8 cc.

The container was surrounded by a silvered pyrex Dewar flask 14 cm. in diameter. The storage cylinder used to keep and weigh the ethane under its saturation pressure was made of stainless steel (Allegheny metal, composition: C less than 0.2%; Cr, 17–20%; Ni, 7–10%; Fe, 70–76%). The weight of the storage cylinder was 690 g. and its volume 360 cc.

Measurements.—Both energy and temperature measurements were made with a White double potentiometer, *A*, Fig. *2*. The electrical connections are shown in Fig. *2*, and were essentially the same as those used by Gibson and Giauque? B indicates the resistance thermometer and C the heater of the calorimeter. **A** constant thermometer current was obtained by discharging six lead storage cells, N, continuously through a 50,000-ohm resistance, J, in series with the thermometer. The potential drop across the 100-ohm standard resistance, H, gives the value of the thermometer current, amounting to about 0.00024 ampere. The e.m.f. of the thermometer was measured directly across its terminals. In order to obtain the heat input, the potential drops across F and O were read; the former gave the current directly while the latter was a known fraction of the total drop. The parallel lead correction and also the correction for heat generated in the lead wires between the calorimeter and copper cylinder were made; the latter was in most cases negligible. Energy was

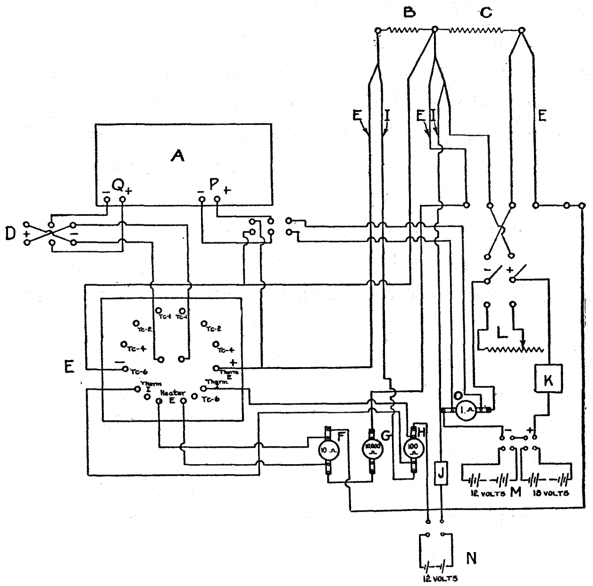

Fig. 2.—Electrical connections of apparatus.

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[9] Onnes and Holst, Comm. *Phys. Lab. Univ. Leiden,* No. 142A (1914).

[10] Meissner, *Ver. deut. phys. Ges., 16,* 262 (1914).

obtained from a set of lead storage batteries, M. The rheostat, L, was used to stabilize the heating current; the ammeter, K, gave its approximate value. E was a mercury master switch, D a mercury reversing switch for thermocouples, and Q and P the two independent circuits of the White double potentiometer. An attempt was made to heat the copper cylinder simultaneously with the calorimeter, but for the runs with the copper calorimeter, this had to be abandoned, since a decided temperature lag was noticed in the cover of the copper cylinder. For the runs with the steel calorimeter an extra heating element was wound around the cover, and the two thermocouples, one near the bottom of the cylinder, and the other at the bottom of the cover, registered a simultaneous rise. Since the rates of heating of the calorimeter and cylinder were not always identical, the heat leak correction for the steel calorimeter was made graphically by plotting the temperatures of the copper block and the outside of the steel calorimeter against time and obtaining the area between the two curves by means of a planimeter; from the area and the rates of heating before and after each run, the heat leak was calculated.

An additional correction discussed by Giauque and Wiebe[11] was not necessary in case of the steel calorimeter, since the temperature difference between calorimeter and copper cylinder remained very nearly the same at all times and a check made by means of the thermocouple inside the well showed no discrepancies in the two temperature rises. The check runs at lower temperatures made with the steel calorimeter did not indicate any discrepancies with respect to the runs made with the copper calorimeter, beyond the experimental error.

For the lowest temperatures liquid nitrogen boiling under reduced pressure was used; otherwise liquid nitrogen, air, oxygen or ethyl bromide cooled by means of liquid nitrogen served as the bath liquid in the Dewar.

The average run lasted ten minutes.

All standard resistances, the standard cell of the potentiometers and the stop-watch were checked by the U. S. Bureau of Standards before and after the measurements.

The stop-watch showed a discrepancy of less than 0.02% for a ten-minute interval between the two calibrations, and we place our accuracy of time measurement at 0.05%. For the heat capacity measurements on the empty calorimeter, hydrogen was introduced in order to speed up the attainment of equilibrium; a small correction was applied to take into account the heat capacity of this gas.

Each batch was weighed when put in and when taken out of the calorimeter. The discrepancy between the two weighings was less than 0.005%.

Temperature Scale.—The thermocouples used were calibrated at approximately ten-degree intervals against platinum resistance thermom-

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[11] W. F. Giauque and R. Wiebe, THIS JOURNAL, 50, 109 (1928).

eter No. 2[12] of the laboratory. The calibration was made in a cryostat described by Walters and Loomis.[13] In their work the boiling point of liquid oxygen was assumed to be −183.00°, while according to the recent international agreement[14] the boiling point has been fixed at −182.97'. We have applied the necessary correction to the melting-point temperature only, since in specific heat determinations we are concerned with temperature differences primarily. The absolute temperature is probably correct to 0.07' except below −185°, where it may or may not be better than 0.10°. The ice point of the resistance thermometer was found to check the original value within the accuracy of the instrument. The copper resistance thermometers were calibrated in place by means of the thermocouples attached to the calorimeter. The calibration was checked repeatedly.

Heat Capacity Data

The results are given in Table I and Fig. 3. The data of Eucken and Hauck lie on a straight line and, therefore, approach our data at low and high

TABLE I

HEAT CAPACITY DATA

Mol. wt., 30.0462. 15° gram calorie, 4.185 joules. Fillings: I, 2.597 moles; II, 2.542; III, 2.050; IV, 1.782; V, 1.540; VI, 1.294. I and II, copper calorimeter; III, IV, V and VI, steel calorimeter. C_{SV}, heat capacity of saturated vapor per mole; C_{SL}, heat capacity of saturated liquid per mole.

T, °K.	Heat cap. of empty cal., cal./deg.	C_{SL}, cal./deg.	$-C_{SV}$, cal./deg.	Filling
67.46	9.81	11.18	..	I
70.64	10.43	11.71	..	II
71.59	10.67	11.99	..	I
73.41	11.06	12.26	..	II
75.67	11.49	12.85	..	I
89.52	Melting point	...	..	...
96.77	14.88	16.35	..	II
96.82	14.88	16.42	..	I
98.06	23.24	16.37	..	III
101.54	15.41	16.41	..	I
107.08	25.43	16.39	..	III
108.65	16.20	16.37	..	II
115.74	16.95	16.40	..	II
116.19	27.46	16.35	..	III
122.70	17.57	16.51	..	II
123.60	17.65	16.52	..	I
128.08	18.03	16.61	..	I
128.49	18.06	16.60	..	II
132.65	18.37	16.68	..	II
138.00	18.78	16.69	..	II
138.18	18.79	16.72	..	I

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[12] Loomis and Walters, THIS JOURNAL, 47, 2851 (1925).

[13] Walters and Loomis, *ibid.*, 47, 2302 (1925).

[14] F. Henning and J. Otto, Z. *Instrumentenk.*, 48,372 (1928).

TABLE I (Concluded)

T, °K.	Heat cap. of empty cal., cal./deg.	C_{SL}, cal./deg.	$-C_{SV}$, cal./deg.	Filling
138.31	31.41	16.68		III
142.43	19.07	16.74		I
143.36	19.14	16.73		II
151.75	19.74	16.71		II
152.60	19.72	16.75		I
154.99	33.60	16.78		III
156.98	19.96	16.78	..	I
157.42	19.98	16.74		II
160.10	20.16	16.98		I
162.65	20.25	17.00		II
164.49	34.57	17.13		III
165.93	20.40	17.03		I
168.09	20.49	17.10		II
170.18	20.57	17.14		I
172.05	20.64	17.14		II
172.69	35.44	17.23		III
178.17	20.81	17.39		II
181.50	36.29	17.45		III
182.03	20.90	17.51		II
184.46	Boiling **point**	...	..	...
190.00	37.04	17.56	5.82	III
199.86	37.82	17.76	5.47	III
208.88	38.48	18.07	5.21	III
212.80	38.74	18.14	5.23	IV
220.48	39.44	18.58	5.07	IV
228.76	39.74	19.25	4.88	IV
236.21	40.18	19.66	5.12	IV
244.61	40.62	20.05	5.80	IV
252.53	41.08	20.81	6.45	IV
258.22	41.34	21.12	7.51	V
265.25	41.66	22.05	8.71	V
273.06	41.96	23.43	10.78	V
278.07	42.12	24.20	13.15	V
284.07	42.31	26.06	16.44	VI
291.27	42.50	29.30	24.51	VI
294.85	42.58	32.43	30.47	VI
305.2	**Critical** point	..	..	..

temperatures. It will be seen from Table II and Fig. **3** that the discrepancies between the values reported by Eucken and Hauck[6] and the values presented here are outside any experimental inaccuracy or impurity. As a matter of fact, it is not thought that their ethane was of higher purity than ours if we take into account the purity of some of the other substances they used and the difficulty of purification. The points in our favor are improved calorimetric design and from 20 to **30** times larger amounts. Since other measurements have been made with the same apparatus and values of other observers have been checked, it is believed that the measurements pre-

TABLE II

HEAT CAPACITY DATA

T, °K.	C_{SL}, Eucken and Hauck	C_{SL}, Wiebe, Hubbard and Brevoort
100	18.0	16.37
110	18.05	16.38
120	18.9	16.44
130	19.3	16.54
140	19.7	16.68
150	20.1	16.83
160	20.60	17.00
170	21.0	17.22
180	21.4	17.38
190	21.8	17.58
200	22.2	17.80
210	22.55	18.14
220	23.0	18.56
230	23.3	19.19
240	23.7	19.71
250	24.1	20.54
260	24.5	21.60
270	25.0	22.96
280	..	24.86
290	..	28.56
295	..	32.54

sented here are the more reliable. The accuracy is estimated to be 0.5% for the liquid below the boiling point and 1% at higher temperatures. The few measurements of solid ethane are probably not more accurate than to within 1 to 2%.

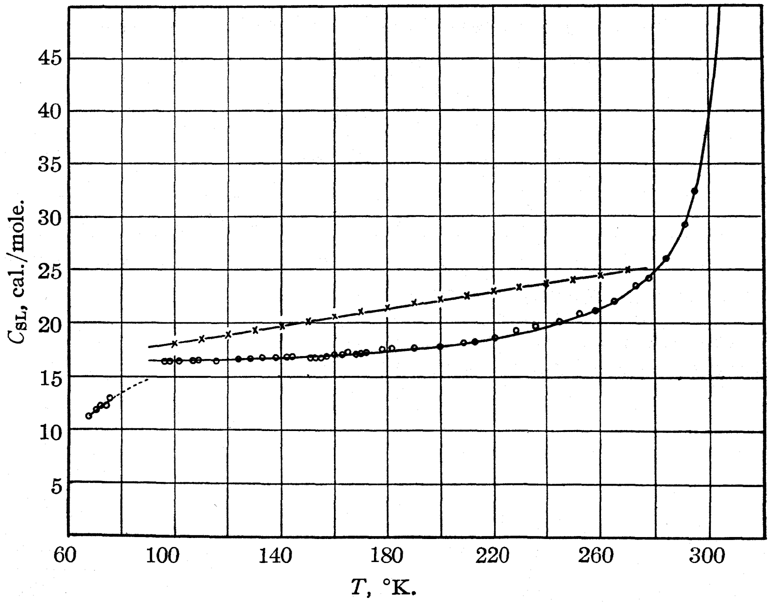

Fig. 3.—Heat capacity in calories per mole of saturated liquid ethane.

The method outlined by Osborne and Van Dusen[15] was used to calculate the heat capacity of the saturated liquid. The heats of vaporization

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[15] N. S. Osborne and M. S. Van Dusen, Sci. Papers, Bureau of Standards, No. **313** **(1917).**

were taken from Porter[6] and from Dana and co-workers.[16] The liquid and vapor densities have been measured by Porter,[5] Kuenen[17] and Maass and McIntosh[18] and Maass and Wright.[19]

The critical data have been summarized by Pickering,[20] who selected the following values for ethane: T_c, 305.2°K.; P_c, 48.8 atm.; d_c, 0.21 g./cc. The following data are given as a typical example for the calculation of the heat capacity.

Sample Calculation.—Potentiometer reading across F, Fig. 2, is 0.0265856 volt.

$$I_{\text{av.}} = \frac{0.0807261 + 0.0807088}{2} = 0.0807175 \text{ amp.}$$

Time, 601.8 sec.

Energy added to calorimeter plus that lost in parallel resistance and lead wires

$$\frac{10014}{10} \times 0.0265856 \times 0.0807175 \times 601.8 \times 0.23895 = 309.017 \text{ cal.}$$

Energy lost in parallel resistance

$$\frac{10014}{10^2} \times (0.0265856)^2 \times 601.8 \times 0.23895 = 10.178 \text{ cal.}$$

Lead wire correction, 0.084 cal.

Energy supplied to calorimeter = 309.017 − 10.178 − 0.084 = 298.755 cal.

Initial resistance 225.9667 ohms. Final resistance 230.4005 ohms

Rate of warming in ohms per minute

Before starting run	0.00103
After close of run when equilibrium was attained	0.00127
Equilibrium period, 10 minutes	

Resistance interval correction calculated graphically from initial and final rates, initial and final temperature differences between calorimeter and surroundings, and special rate determinations

Correction for period during the run, ohms	0.0193
Correction for equilibrium period, ohms	0.0127
	0.0320
Initial temperature, °C.	−30.551
Final temperature, °C.	−26.602
Uncorrected temperature rise, °C.	3.949
Temperature interval correction	−.028
Corrected temperature rise	3.921

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[16] L. I. Dana, A. C. Jenkins, J. N. Burdick and R. C. Timm, *Refrig. Eng.*, 12, 387 (1926).

[17] Kuenen, *Phil. Mag.*, 40, 173 (1895).

[18] Maass and McIntosh, THIS JOURNAL, 36, 737 (1914).

[19] Maass and Wright, *ibid.*, 43, 1098 (1921).

[20] S. F. Pickering, *J. Phys. Chem.*, **28**, 97 (1924).

Total heat input per degree, 298.755/3.921 = 76.215	76.215 cal.
Heat capacity of empty calorimeter	40.650 cal.
Difference	35.565 cal.
Weight of ethane, g.	53.534
Moles of ethane	1.7817
Heat capacity of ethane 35.565/1.7817	19.96 cal.
Correction for vapor present	0.09 cal.
Corrected heat capacity per mole of ethane	20.05 cal.
Average temperature	244.61°K.

The heat capacities of the saturated vapor and liquid C_{SV} and C_{SL} are defined as follows

$$C_S = C_P - T\left(\frac{\partial v}{\partial T}\right)_P \frac{dP}{dT_{sat.}}$$

TABLE III

ENTROPY AND HEAT CONTENT DATA

$$S_L = \int_{184.46}^{T} dQ/T\,dT = \int_{184.46}^{T} C_{SL}/T\,dT = \text{entropy of liquid}$$

$$S_V = S_L + L/T = \text{entropy of vapor}$$

T, °K.	S_L cal./deg. per mole	L/T	S_V cal./deg./mole
184.46	0.0000	18.03	18.03
185	.0510	17.96	18.01
190	.5181	17.33	17.85
195	.9747	16.71	17.69
200	1.424	16.13	17.55
205	1.862	15.57	17.43
210	2.297	14.99	17.29
215	2.726	14.44	17.17
220	3.149	13.92	17.07
225	3.570	13.37	16.94
230	3.988	12.85	16.84
235	4.403	12.33	16.73
240	4.817	11.79	16.61
245	5.230	11.28	16.51
250	5.644	10.74	16.39
255	6.052	10.19	16.24
260	6.462	9.64	16.10
265	6.876	9.08	15.95
270	7.293	8.48	15.77
275	7.720	7.85	15.57
280	8.156	7.19	15.35
285	8.607	6.48	15.08
290	9.082	5.65	14.73
295	9.601	4.68	14.29
300	10.200	3.41	13.61
305.2	11.95	0.00	11.95

TABLE IV

ENTROPY AND HEAT CONTENT DATA

T, °K.	H_L, heat content of liquid, cal./mole	L, heat of vapor, cal. per mole	H_V, heat content of vapor, cal./mole
184.46	0.0	3325	3325
190	97.7	3292	3390
195	186.3	3258	3444
200	275.7	3226	3502
205	365.9	3187	3553
210	457.1	3149	3605
215	549.3	3106	3655
220	642.6	3060	3703
225	737.3	3007	3744
230	833.4	2954	3788
235	931.3	2894	3825
240	1031.0	2830	3861
245	1133	2760	3893
250	1239	2684	3923
255	1344	2600	3944
260	1455	2507	3962
265	1568	2398	3966
270	1685	2290	3975
275	1806	2151	3957
280	1933	2014	3947
285	2067	1840	3907
290	2211	1638	3849
295	2370	1381	3751
300	2540[a]	1026	3566[a]
305.2	3050[a]	0	3050[a]

[a] Extrapolated values.

Since C_{SL} was measured, C_{SV} was calculated from the Clausius relation

$$C_{SV} - C_{SL} = \frac{dL}{dT} - \frac{L}{T}$$

where L is the heat of vaporization. In order to calculate the temperature coefficient of the heat of vaporization, the following equation was found satisfactory

$$L = 483.2\,(T_c - T)^{1/2} - 16.45\,(T_c - T)$$

The entropy and heat content of the saturated liquid and vapor are given in Tables III and IV and Figs. 4 and 5. The normal boiling point of ethane, 184.47°K., was taken as zero for both the entropy and heat content. The heat content is defined by the equation

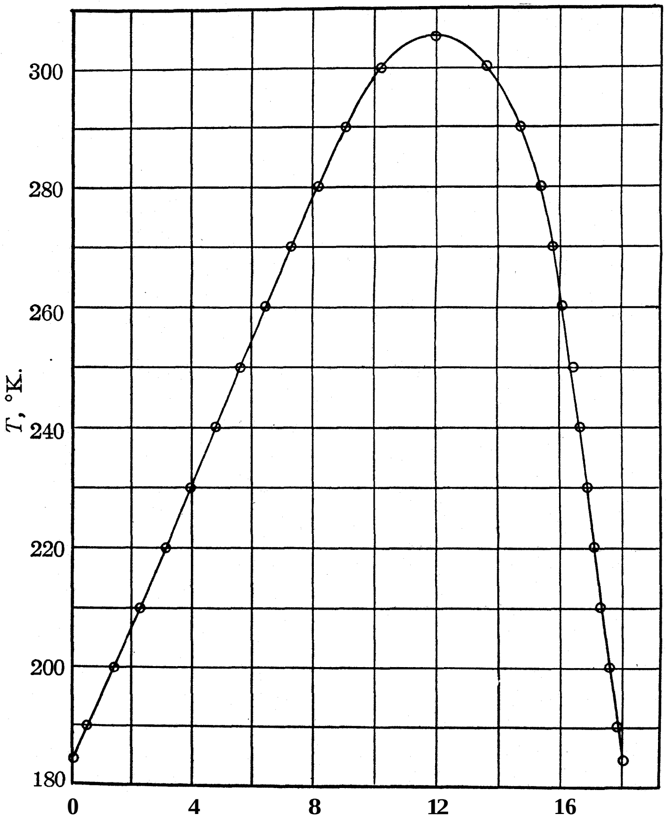

Fig. 4.—Temperature-entropy diagram for ethane.

$$H = E + pv$$

where E is the internal energy of the system.

As will be seen in the Table, C_{SV} is negative. A general rule for ascertaining whether a substance has positive or negative values of C_{SV} cannot be given, but approximate calculations by van der Waals[21] show that in the case of mono-, di- and triatomic substances a positive value of C_{SV} is entirely excluded, while substances with more than three atoms may have positive values over part of the range before and after which they are negative. Ether is an example showing positive values for the heat capacity of the saturated vapor.

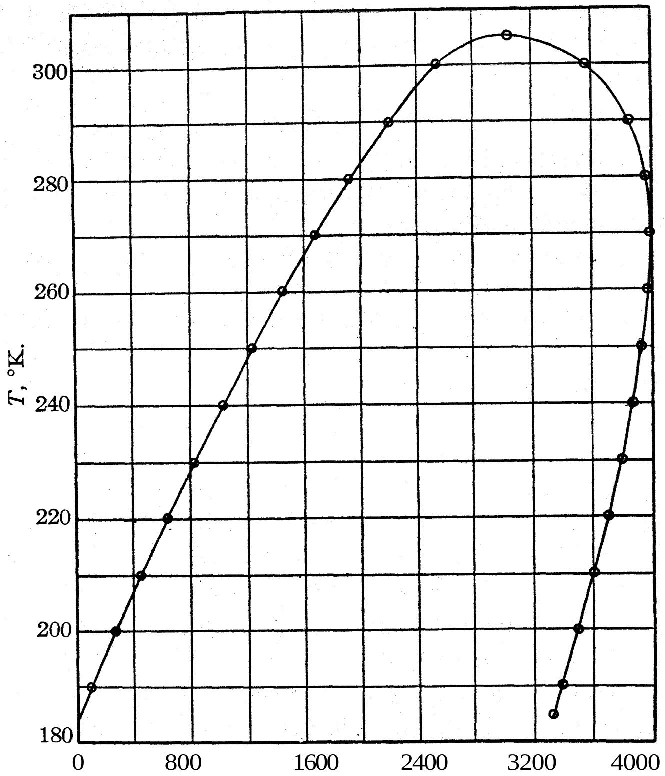

Fig. 5.—Mollier diagram for ethane.

Heat of Fusion and Melting Point.—The amount of heat consumed in premelting below the initial temperature of the run was determined graphically in each case and added as a correction to the heat of fusion. Table V gives the results of six determinations.

TABLE V

HEATS OF FUSION

Initial T, °K.	86.97	87.84	88.52	87.47	86.68	86.41
Final T, °K.	90.37	91.63	92.02	90.37	91.10	90.79
Heat of fusion, cal./mole	665.2	666.6	665.3	669.1	669.8	668.7

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[21] Van der Waals-Kohnstamm, "Lehrbuch der Thermodynamik," Vol. I, p. 70.

The average value of the heat of fusion is 667.5 ± 3 cal. per mole of ethane. The melting point was found to be −183.65 ± 0.10°C. Ladenburg and Krügel[22] give −172.1° and Lebeau[23] remarks that ethane is still liquid at −195°.

We wish to express appreciation to Dr. C. W. Kanolt, formerly in charge of the Cryogenic Laboratory, Bureau of Mines, for the interest he has shown in our work, and to thank Messrs. Rowe and Schmidt of the instrument shop of the Pittsburgh Station for their excellent construction of the apparatus used in this study.

Summary

One low-pressure and one high-pressure calorimeter for determinations of heat capacities of liquids below room temperatures under their saturation pressure have been described.

Measurements of the heat capacity of saturated liquid ethane and the heat of fusion are presented.

Calculations of the entropy and heat content of the saturated liquid and vapor have been made.

AMARILLO, TEXAS

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE]

THE HEAT CAPACITY OF SATURATED LIQUID NITROGEN AND METHANE FROM THE BOILING POINT TO THE CRITICAL TEMPERATURE[1]

BY R. WIEBE[2] AND M. J. BREVOORT[3]

RECEIVED OCTOBER 14, 1929 PUBLISHED FEBRUARY 6, 1930

Three papers have recently been published on the thermodynamic properties of nitrogen.[4,5,6] Since large discrepancies exist between the results of the different workers, it was thought desirable to obtain accurate experimental values in order to decide the question.

Keesom and Houthoff[5] have recently prepared temperature–entropy and Mollier charts of methane utilizing the results of Keyes, Smith and

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[22] A. Ladenburg and C. Krügel, Ber., **33**, 637 (1900).

[23] Lebeau, *Compt. rend.*, 140, 1456 (1905).

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Physical Chemist, Helium Division. U. S. Bureau of Mines.

[3] Assistant Physicist, Helium Division, U. S. Bureau of Mines.

[4] Worth H. Rodebush, John W. Andrews and John B. Taylor, THIS JOURNAL, 47, 313 (1925).

[5] W. H. Keesom and D. J. Houthoff, *Comm. Phys. Lab. Univ. Leiden*, Suppl. No. 65.

[6] Russell W. Millar and John D. Sullivan, U. S. Bureau of Mines, Technical Paper 424.

Joubert.[7] Their work involves several uncertainties due to lack of data, and confirmation was needed.

No heat capacity measurements of saturated liquid nitrogen or methane above 1 atmosphere were in existence, but several observers[8] have made determinations up to the boiling point. Their data have been incorporated for comparison.

Nitrogen and methane are two of the main constituents of helium-bearing natural gas, and it is of importance to know accurately their thermal behavior.

Preparation.—The purest commercial nitrogen available was used as crude material. The gas was passed successively through tightly packed copper leaf heated to about 350°, fused potassium hydroxide and phosphorus pentoxide. The liquefied gas was fractionated several times, the first and last portions being rejected each time.

Two different batches of methane were prepared. The Grignard method was used for the first. Dry methyl iodide in small quantities was added to fresh turnings from an ingot of magnesium in an excess of dry ether. The heat of reaction caused the ether to boil, and the vapors were condensed by means of a water-cooled reflux condenser placed vertically above the flask. A calcium chloride tube at the top of the condenser prevented the entrance of moisture. Water was then added to decompose the Grignard reagent, and the methane given off was passed successively through a condensation bulb to eliminate the ether, fuming sulfuric acid, concentrated sulfuric acid, 30% sodium hydroxide solution, potassium hydroxide sticks and phosphorus pentoxide. The liquefied gas was then ,fractionated several times, the first and last portions being rejected each time, The second batch was prepared by the method outlined by Gladstone and Tribe? who prepared methane by the action of a copper–zinc couple on methyl iodide. The gas was purified in the same way as in the Grignard method. The melting point was determined to be **–182.9** ± 0.1°; a slight variation indicated some impurity. The value given in "International Critical Tables" is –184°.

Measurements.—The apparatus used has been described in detail in a previous paper.[10] The measurements were made in the steel calorimeter exclusively. The method outlined by Osborne and Van Dusen[11] was used

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[7] F. G. Keyes, L. B. Smith and D. B. Joubert, **J.** *Math. Phys. Mass. Inst. Tech.*, *1,* **211 (1922).**

[8] Klaus Clusius, Z. *physik Chem.*, **3B, 41 (1929).** In this article Clusius criticizes the temperature scale used by W. F. Giauque and R. Wiebe in their work on the heat capacity of hydrogen chloride [THIS JOURNAL, 50, **109** (1928)]. The authors of the latter article wish to call attention again to the passage on page **111:** "However, since the results deviate in only one direction, it is improbable that the difficulty can be due primarily to inaccurate temperature scale. Even an approximate knowledge of the extremes of the temperature range investigated would mean that if some results were too high, others would necessarily be made too low." In other words, if the extremes of the temperature range are known accurately and the size of the "degrees" is incorrect, it follows that some "degrees" must be too small and some too large and, therefore, some measurements too low and some too high.

[9] J. H. Gladstone and Alfred Tribe, **J.** *Chem. Soc.*, **45,154 (1884).**

[10] **R.** Wiebe, K. H. Hubbard and M. J. Brevoort, THIS JOURNAL, 52, **611 (1930).**

[11] Nathan **S.** Osborne and Milton S. Van Dusen, Sci. Papers, Bureau of Standards, No. **313.**

in making the necessary corrections in order to obtain the heat capacity of the saturated liquid. The gases were weighed in a steel cylinder at about 60 atmospheres' pressure. The average error is estimated to be about 1%; a few points are off slightly more, but all the rest fall well within this limit when a smooth curve is drawn through the results. The probable distribution of the percentage error is as follows

Weighing	0.1	Heat leak correction	0.1
Time measurement	0.1	Vapor space correction	0.1
Temperature interval	0.5	Heat cap. of empty calorimeter	0.1

The thermocouples were calibrated against the platinum resistance thermometer No. 2.[12]

TABLE I

NITROGEN

Fillings: I, 23.88 moles; II, 2.900; III, 2.611; IV, 2.297; V, 1.908. S_{SL}, heat capacity of the saturated liquid per mole. Molecular weight, 28.016. 15° gram calorie, 4.185 joules.

T, °K.	Heat cap. of empty calorimeter	C_{SL}, cal/deg.	Observer	Filling
63.95		13.34	Keesom and Onnes	
64.6		13.15	Eucken	
65.0		13.22	Eucken	
66.9		13.54	Clusius	
67.5		13.28	Eucken	
68.2		13.25	Eucken	
68.4		13.64	Clusius	
69.15	. .	13.40	Keesom and Onnes	
69.73		13.28	Keesom and Onnes	
70.2	...	13.63	Clusius	
71.8		13.66	Clusius	
72.7	. .	13.33	Eucken	
73.5	...	13.69	Clusius	
75.46	. .	13.74	Keesom and Onnes	
76.49		12.96	Keesom and Onnes	
79.17	18.09	13.76	Wiebe and Brevoort	I
82.64	19.08	13.95	Wiebe and Brevoort	I
89.50	20.95	14.16	Wiebe and Brevoort	II
95.39	22.54	14.50	Wiebe and Brevoort	II
95.46	22.36	14.71	Wiebe and Brevoort	III
99.55	23.60	15.04	Wiebe and Brevoort	III
103.31	24.53	15.63	Wiebe and Brevoort	IV
103.72	24.64	15.56	Wiebe and Brevoort	III
107.22	25.47	15.99	Wiebe and Brevoort	III
107.48	25.52	16.10	Wiebe and Brevoort	IV
111.57	26.46	17.30	Wiebe and Brevoort	IV
112.97	26.76	17.60	Wiebe and Brevoort	V
115.25	27.25	18.27	Wiebe and Brevoort	IV
116.99	27.62	18.72	Wiebe and Brevoort	V

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[12] Loomis and Walters, THIS JOURNAL, 47, 2851 (1925).

TABLE II

METHANE

Fillings: I, 2.959 moles; II, 2.509; III, 1.789; IV, 1.148; V, 1.803. I, II, III and IV from first batch; V from second batch.

T, °K.	C_{SL}, cal./deg.	Observer	Filling
95.4	12.81	Clusius	
96.25	13.65	Eucken and Karwat	
97.3	13.52	Eucken and Karwat	
97.7	12.85	Clusius	
97.73	12.94	Wiebe and Brevoort	I
98.9	12.90	Clusius	
99.2	13.46	Eucken and Karwat	
102.0	12.97	Clusius	...
102.27	13.09	Wiebe and Brevoort	I
103.2	13.43	Eucken and Karwat	. .
103.9	13.43	Eucken and Karwat	..
105.3	13.01	Clusius	...
107.2	13.49	Eucken and Karwat	...
108.7	13.59	Eucken and Karwat	...
110.94	13.20	Wiebe and Brevoort	I
117.53	13.27	Wiebe and Brevoort	I
121.82	13.26	Wiebe and Brevoort	I
129.32	13.77	Wiebe and Brevoort	I
134.28	14.05	Wiebe and Brevoort	I
140.49	14.34	Wiebe and Brevoort	II
149.51	14.78	Wiebe and Brevoort	II
153.70	14.97	Wiebe and Brevoort	II
154.75	15.27	Wiebe and Brevoort	III
160.96	16.01	Wiebe and Brevoort	III
169.02	17.30	Wiebe and Brevoort	III
174.75	19.48	Wiebe and Brevoort	V
178.00	20.90	Wiebe and Brevoort	IV
180.86	22 18	Wiebe and Brevoort	V
182.82	23.92	Wiebe and Brevoort	IV
182.95	24.18	Wiebe and Brevoort	III
184.43	26.01	Wiebe and Brevoort	V
188.24	52.34	Wiebe and Brevoort	IV
191.03	Critical temperature		

Heat Capacity Data.—The following definitions are used in this article, subscripts L and V referring to the liquid and vapor state, respectively. C_S = heat capacity of the saturated state per mole; H = heat content per mole; S = entropy per mole and L = heat of vaporization per mole. Thermodynamics gives the following relations between these quantities

$$C_S = C_P - T\left(\frac{\partial v}{\partial T}\right)_P \frac{dP}{dT_{sat.}} = C_P - \left(\frac{\partial v}{\partial T}\right)_P \frac{L}{\Delta v}$$

$$H = E + pv \qquad S_L = \int \frac{C_{SL}}{T}\,dT \qquad S_V = S_L + L/T$$

The results are shown in Table I and II and are plotted in Figs. 1 and 2.

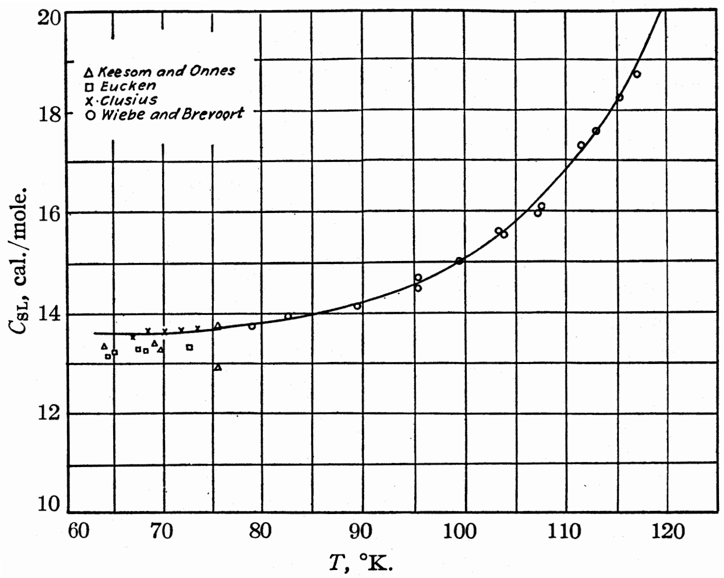

Fig. 1.—Heat capacity of saturated liquid nitrogen.

The measurements of previous investigators[8] have been included. Our extrapolated curve for nitrogen passes well through the values of Clusius and one point of Keesom and Onnes. The other points of the latter and

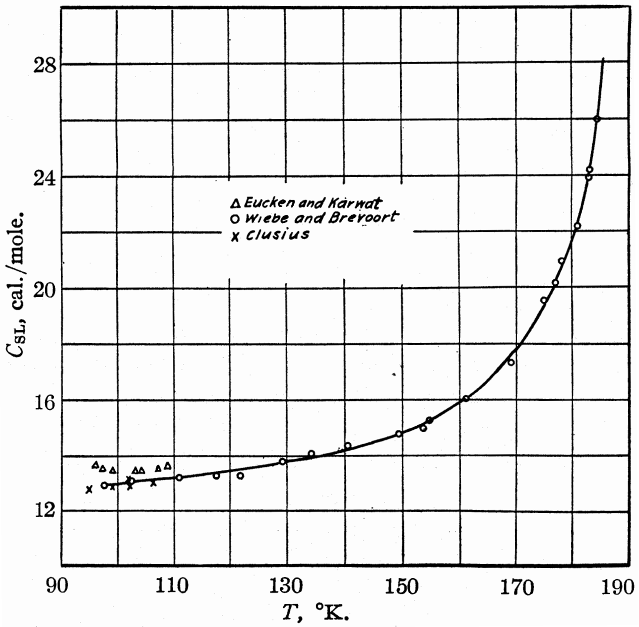

Fig. 2.—Heat capacity of saturated methane.

of Eucken are slightly lower. In case of methane, we also check the results of Clusius, while the determinations of Eucken and Karwat are too high.

Heat Content and Entropy.—Tables III and IV show the calculations made from the experimental data of the authors.

TABLE III

NITROGEN

Heat content/mole in cal.

T	$\int_{77.4}^{T} C_{SL} dT$	$\int v dp$	H_L	L	H_V
77 4	0.0	. . .	0.0	1335	1335
80	34.81	0.31	35.1	1314	1349
85	103.87	1.09	105.0	1265	1370
90	174.39	2.24	176.8	1213	1390
95	246.49	3.88	250.4	1161	1411
100	320.87	6.15	327.0	1102	1429
105	398.25	9.20	407.5	1028	1435
110	479.61	13.26	492.9	933	1426
115	566.45	18.60	585.1	806	1391
120	661.74	24 94	686 7	622	1308
125	. . .	. . .	870^a	257	1137"
126	. . .	. . .	1005"	0	1005^a

^{a} Extrapolated values.

TABLE IV

METHANE

Heat content/mole in cal.

T	$\int_{100}^{T} C_{SL} dT$	$\int v dp$	H_L	L	H_V	H_{50}
100	0.0	0.00	0.0	2048	2048	1024
105	64.5	.20	65.7	2015	2081	1073
110	131.3	.48	131.8	1983	2115	1123
111.5	151.6	.59	152.2	1972	2124	1138
115	197.8	.89	198.7	1950	2149	1174
120	264.8	1.43	266.3	1917	2183	1224
125	332.5	2.16	334.7	1883	2218	1276
130	401.4	3.10	404.6	1847	2251	1327
135	470.9	4.30	475.2	1808	2283	1379
140	541.3	5.80	547.1	1767	2314	1430
145	612.9	7.65	620.2	1721	2341	1480
150	686.0	9.92	696.0	1670	2366	1531
155	761.3	12.67	774.0	1612	2386	1580
160	839.1	15.99	855.1	1546	2401	1628
165	920.3	19.95	940.2	1470	2410	1675
170	1006.1	24.65	1030.7	1382	2413	1722
175	1098.4	30.28	1128.7	1276	2405	1767
180	1201.6	37.00	1238.6	1141	2380	1809
185	1321.2	45.13	1366.3	939	2306	1836
191.03			1840^a	0	1850^a	1850^a

^{a} Extrapolated values.

The heats of vaporization for nitrogen were taken from a smooth curve drawn through the values given by Burnett[13] and Keesom and Houthoff.[14] Near the boiling point we inclined toward the values of the former, since the heat of vaporization at the boiling point has been determined experimentally,[15] while at higher temperatures the values of Keesom and Houthoff appeared to us more reasonable with regard to entropy and heat content especially at 125°K.

The densitites of the co-existing phases for nitrogen have been determined by Mathias, Kammerlingh Onnes and Crommelin.[16] The heats of vaporization and densities of the co-existing phases for methane were taken from the work of Keyes, Smith and Joubert.[7] Pickering[17] has summarized the critical constants of various gases obtained by different observers and selected the following values for nitrogen and methane.

	Nitrogen	Methane
T_c, °K.	126.0	190.6
P_c, atm.	33.5	45.7
d_c, g./cc.	0.3110	0.162

In Table V and Fig. 3, a comparison is made between the heat content values

TABLE V

NITROGEN

Heat Content in 15° cal./mole

Abbreviations: M. & S , Millar and Sullivan; B , Burnett; K. & M., Keesom and Houthoff; W. & B., Wiebe and Brevoort.

T, °K.	H_L, M. & S.	H_L, B.	H_L, K. & H.	H_L, W. & B.	H_V, M. & S.	H_V, B.	H_V, K. & H.	H_V, W. & B.	H_{50}, W. & B.
77.4	0.0	0.0	0.0	0.0	1335	1336	1317	1336	668
80	39	34.5	33.3	35.1	1352	1348	1329	1349	692
85	115	102.0	97 2	105.0	1381	1368	1350	1370	734
90	189	170.6	160.8	176.8	1402	1383	1370	1390	783
95	257	2392	225.3	250.4	1412	1394	1387	1411	830
100	326	310.0	295.9	327.0	1412	1398	1399	1429	878
105	393	383.5	376.5	407.5	1402	1394	1406	1435	922
110	460	461.3	471.8	492.9	1379	1379	1404	1426	959
115	534	547.2	586.7	585.1	1338	1350	1387	1391	988
120	625	650.5	732 3	686.7	1269	1294	1345	1308	998
125	781	823.6	962.1	870[a]	1112	1154	1214	1137[a]	...
126	952	990.4	1106	1005[a]	952	990.4	1106	1005[a]	1000[a]

[a] Extrapolated values.

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[13] E. S. Burnett, unpublished report to the U. S. Bureau of Mines; see Millar and Sullivan, Ref. 6.

[14] Professor Keesom has kindly sent us his values for comparison, see Ref. 5.

[15] Heinrich Alt, *Ann. Physik,* [4] **19,** 639 (1906); L. I. Dana, *Proc. Am. Acad. Arts Sci.,* 60, 241 (1926).

[16] E. Mathias, H. Kammerlingh Onnes and C. A. Crommelin, *Comm. Phys. Lab., Univ. Leiden,* No. 145c (1914).

[17] S. F. Pickering, *J. Phys. Chem.,* **28,** 97 (1924).

obtained by Millar and Sullivan,[6] Burnett,[13] Keesom arid Houthoff[4] and the authors for nitrogen.

Burnett had obtained his values frotn two empirical equations expressing the heat content along the 50% quality line

$$H_{50} = 1090 - 1.5486\,(T_c - T)^{1.375}$$

and the heat of vaporization

$$L = H_V - H_L = 331\,(T_c - T)^{0.375} - 0.404\,(T_c - T)^{1.375}$$

The former was arrived at by adjusting values derived from Keyes' equation of state in the neighborhood of the critical point to conform to the known behavior of other gases and thus obtaining values for the change in heat content between different P–T points in the superheat field and the

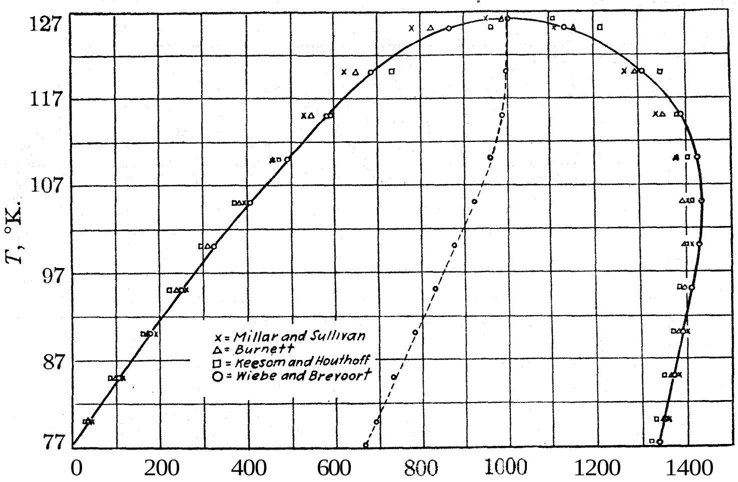

Fig. 3.—Mollier diagram for nitrogen.

TABLE VI

NITROGEN

T, °K.	T_L, cal./deg./mole	L/T	S_V, cal./deg./mole
77.4	0.0	17.25	17.25
80	0.451	16.42	16.87
85	1.295	14.88	16.17
90	2.098	13.48	15.58
95	2.877	12.22	15.10
100	3.635	11.02	14.66
105	4.393	9.79	14.18
110	5.142	8.48	13.62
115	5.925	7.01	12.94
120	6.727	5.18	11.91
125	8.28	2.06	10.34
126	9.32	0.00	9.32

corresponding points on the saturation curve. By combining the two equations of Burnett, we obtain

$$H_V = [1090 - 1.5486\,(T_c - T)^{1.375}] + [165.5\,(T_c - T)^{.375} - 0.202\,(T_c - T)^{1.375}]$$
$$H_L = [1090 - 1.5486\,(T_c - T)^{1.375}] - [165.5\,(T_c - T)^{.375} - 0.202\,(T_c - T)^{1.375}]$$

Burnett chose 70°K. as his reference zero, and we subtracted $H_L\,77.4 - H_L\,70$ from his values. We have given two values for the heat content at the critical point; one was obtained by completing the dome plotted from the H_L and the H_V values against temperature, while the other and probably more correct value was found by extrapolating the heat content of the 50% quality line.

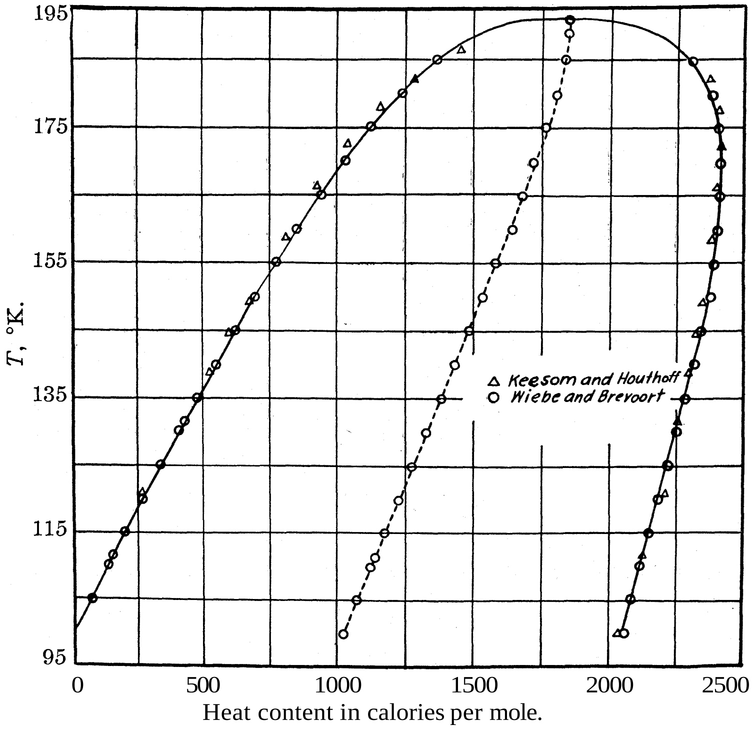

Fig. 4.—Mollier diagram for methane.

Figure 4 shows a comparison between the heat content values of Keesom and Houthoff and those calculated from our experimental data. The agreement is good except in the neighborhood of the critical point, where their values deviate slightly.

Tables VI and VII give the entropy values calculated from our experimental values and Table VIII and Fig. 5 give a comparison between the values of Millar and Sullivan, Keesom and Houthoff, Rodebush, Andrews and Taylor and the authors for nitrogen.

Table VII

Methane

Entropy in cal./deg./mole

T, °K.	S_L, entropy of satd. liquid	L/T, entropy of vaporization	S_V, entropy of satd. vapor
100	0.000	20.48	20.48
105	.641	19.19	19.84
110	1.246	18.03	19.27
111.5	1.431	17.68	19.11
115	1.844	16.96	18.80
120	2.406	15.98	18.38
125	2.962	15.06	18.02
130	3 509	14.21	17.72
135	4.042	13.39	17.44
140	4.563	12.62	17.18
145	5.072	11.87	16.94
150	5.569	11.13	16.70
155	6.051	10.39	16.45
160	6.549	9.66	16.21
165	7.052	8.91	15.96
170	7.568	8.13	15.70
175	8.103	7.29	15.40
180	8.680	6.34	15.02
185	9.327	5.08	14.40
191.03	11.92	0	11.92

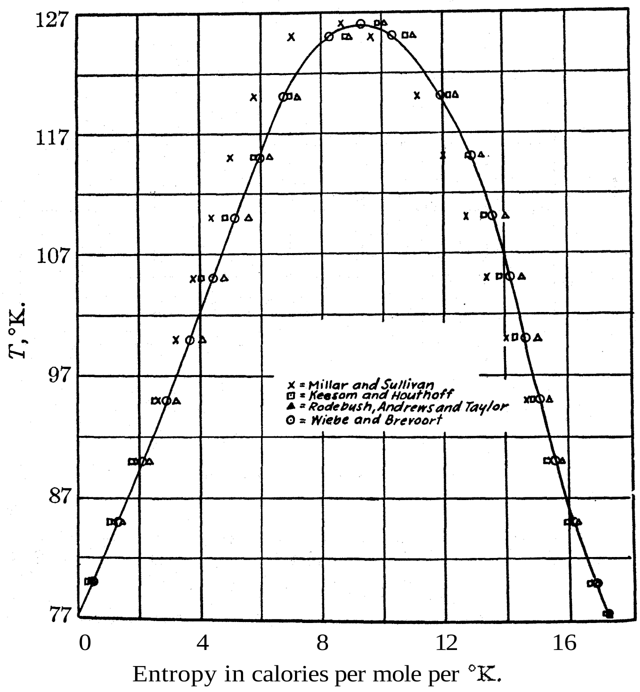

Fig. 5.—Temperature–entropy diagram for nitrogen.

TABLE VIII

NITROGEN

T, °K.	S_L, M. & S.	S_L, K. & H.	S_L, R., A. & T.	S_L, W. & B.	S_V, M. & S.	S_V, K. & H.	S_V, R., A. & T.	S_V, W. & B.
77.4	0.0	0.0	0.0	0.000	17.25	17.17	17.25	17.25
80	0.42	0.36	0.48	0.451	16.83	16.70	16.90	16.87
85	1.18	1.04	1.39	1.295	16.08	15.94	16.27	16.17
90	1.90	1.77	2.28	2.098	15.38	15.33	15.76	15.58
95	2.56	2.52	3.16	2.877	14.72	14.79	15.38	15.10
100	3.21	3.22	4.01	3.635	14.07	14.32	15.03	14.66
105	3.81	4.01	4.75	4.393	13.43	13.84	14.54	14.18
110	4.39	4.82	5.56	5.142	12.74	13.36	14.04	13.62
115	5.01	5.77	6.27	5.925	11.99	12.86	13.28	12.94
120	5.78	6.92	7.15	6.727	11.14	12.16	12.33	11.91
125	7.22	8.84	8.89	8.28	9.64	10.85	10.95	10.34
126	8.67	9.90	10.01	9.32	8.67	9.90	10.01	9.32

Entropies of the vapor by Rodebush, Andrews and Taylor were calculated by adding our entropies of vaporization to their liquid entropies taken from a smooth curve through their data.

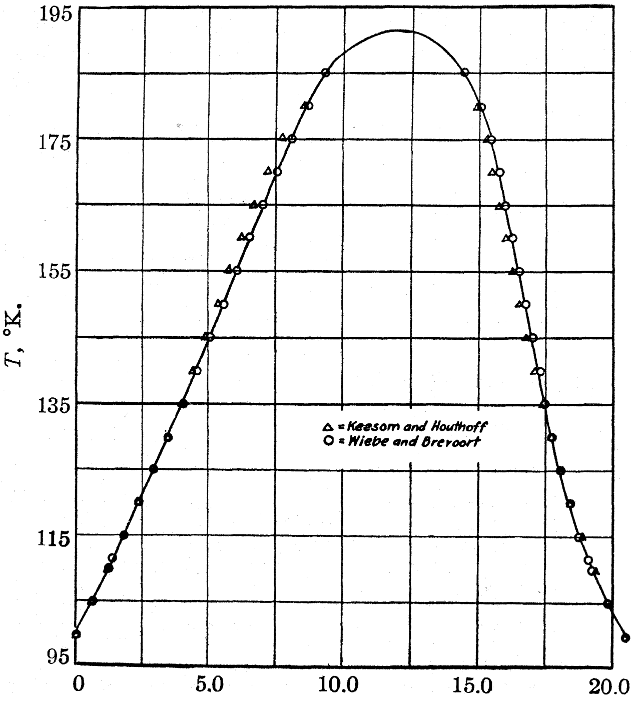

Fig. 6.—Temperature–entropy diagram for methane.

The results of Rodebush, Andrews and Taylor seem to indicate that their vapor was contaminated with liquid spray, which made their percentages too high. A more efficient baffle system would probably reduce or even eliminate the danger of contamination.[18] The entropy values of Keesom and Houthoff and the authors are shown in Fig. 6.

The authors wish to express their appreciation to Mr. G. St. J. Perrott, Superintendent of the Pittsburgh Experiment Station, U. S. Bureau of Mines, and to Dr. David F. Smith of the physical chemistry section for permitting the work of this investigation to be carried out at the Pittsburgh Station.

Summary

The specific heats of saturated liquid nitrogen and methane from the boiling point to the critical temperature have been measured.

The entropy and heat content of the saturated state have been calculated.

AMARILLO, TEXAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF UTAH]

THE COMPOSITION OF CONSTANT BOILING HYDROCHLORIC ACID AT PRESSURES OF 50 TO 1220 MILLIMETERS[1]

BY WALTER D. BONNER AND ALBERT C. TITUS

RECEIVED OCTOBER 15, 1929 PUBLISHED FEBRUARY 6, 1930

Since Hulett and Bonner[2] published their paper on the preparation of standard hydrochloric acid solutions from constant boiling hydrochloric acid, their acidimetric standard has been checked by others, and its use has become fairly common.[3]

However, the only precise determinations of the compositions of these acids so far published are those made near sea level, and those made at the rather low barometric pressures near 640 mm.[4] The experiments of Roscoe and Dittmar, published 70 years ago,[5] remain the only work covering a considerable range of pressures. We have, therefore, determined the compositions and densities of various hydrochloric acids of constant boiling point between the pressures of 50 and 1220 mm. The procedure used was much that of Foulk and Hollingsworth[4] except that the pressure control apparatus was filled with mercury rather than with water. The compositions were determined gravimetrically, by means of silver chloride. The silver nitrate used was very carefully purified. The

[18] This was suggested to the authors by Mr. E. S. Burnett.

[1] Arranged from the Master's Thesis of Albert C. Titus, University of Utah.

[2] Hulett and Bonner, THIS JOURNAL, 31, 390 (1909).

[3] See Morey, *ibid.*, 34, 1027 (1912); Hendrixson, *ibid.*, 37, 2352 (1915); Popoff, "Quantitative Analysis," P. Blakiston's Sons, Philadelphia, 1927, 2d ed., p. 98.

[4] Foulk and Hollingsworth, THIS JOURNAL, 45, 1220 (1923); Bonner and Branting, *ibid.*, 48, 3093 (1926).

[5] Roscoe and Dittmar, Ann, 112, 343 (1859); J. *Chem. Soc.*, 12, 128 (1860); Roscoe, Ann., 116, 213 (1860).

acid sample for each analysis was weighed, the samples being such that the weight of silver chloride was always about 2 g. The total volume of mother liquor and washings was always less than 1 liter, under which condition the correction to be made for dissolved silver chloride is negligible.[6] All weighings are reduced to vacuum and the weights used were carefully calibrated. The compositions given are each the mean of at least three concordant analyses, and the maximum deviation from the mean is never greater than 0.05%. They agree remarkably well with those given by Foulk and Kollingsworth[4] for 760-mm. pressure, and with those previously presented from this Laboratory for 640 mm.[4]

Densities were determined at 25 ± 0.02°, by means of an Ostwald–Sprengel type of pyknometer. The densities given are the means of never fewer than three independent experiments, and are precise to 0.01%. There is, however, a discrepancy of 0.1% between the density given here for the 640 mm. acid, and that given in the paper already referred to, for the same acid. We are unable to assign a cause for this, but we are convinced that the error lies in the previous data. Our density for the 760 mm. acid agrees within less than 1 part in 5000 with that given by Hulett and Bonner for the same acid. The barometer used was carefully compared with the U. S. Weather Bureau instrument in Salt Lake City. All necessary corrections have been applied, both to the barometer and to the pressure control apparatus. Pressures were maintained constant to within 1 mm. The following table gives the data assembled.

TABLE I

DENSITIES AND COMPOSITIONS

Pressure, mm.	Density	HCl, %	Pressure, mm.	Density	HCl, %
50	1.1118	23.42'	600	1.0980	20.638[b]
150	1.1073	22.520[b]	640	1.0973	20.507
250	1.1042	21.883	700	1.0966	20.360[b]
350	1.1019	21.437	760	1.0959	20.222[b]
400	1.1010	21.235[b]	800	1.0955	20.155
450	1.1002	21.075[b]	1000	1.0933	19.734
500	1.0993	20.916	1220	1.0915	19.358
540	1.0987	20.777"			

[a] Result of a single analysis. [b] Interpolated.

When the percentage of hydrochloric acid in these acids is plotted as abscissas, using the corresponding densities as ordinates, the resulting graph is a straight line whose equation is

$$x = \frac{Y - 0.9966}{0.004912}$$

This equation is precise to about 0.05% within the range of ordinary barometric pressures. It is thus possible to prepare a sample of constant boiling hydrochloric acid at any convenient atmospheric pressure, deter-

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[6] See Richards and Wells, THIS JOURNAL, 27, 486 (1905).

mine its density at 25°, and at once compute its hydrochloric acid content with a precision sufficient for any ordinary volumetric work. Any reference to the pressure of the distillation is thus avoided, it being only necessary to see that the barometric pressure is not changing rapidly during the preparation of the constant boiling acid.

Foulk and Hollingsworth, in the work already cited, found that the composition of the constant boiling acid was influenced markedly bv the rate of the distillation. We have been unable to corroborate this. We have made, at various pressures, series of distillations in which the rate was varied from 1.7 cc. to 4.9 cc. per minute. These distillates were compared by determining the densities, and in no case did we find *a* difference in density as great as 1 part in 10,000. For example, in a set of ten such distillates, the mean density was 1.09709, with an average deviation of 0.00004 and a maximum deviation of 0.00009. We would conclude that the rate of distillation has a negligible effect on the composition. However, for the sake of convenience, we carried out all of our distillations at the uniform rate of 4.5 cc. per minute.

Résumé

We have determined the composition and density of constant boiling hydrochloric acid between pressures of 50 and 1220 mm.

We have given an equation by the aid of which the composition of any constant boiling hydrochloric acid may be computed from its density, at 25". The use of this acid as a primary standard in acidimetry is thus simplified.

SALT LAKE CITY, UTAH

NOTES

An Inorganic Stopcock Lubricant.—Up to the present time there has been no inorganic material discovered which compares favorably in all respects with stopcock grease, although there are many types of research in which such a material would be extremely valuable. The two main makeshift substitutes which have been used are moist phosphorus pentoxide and moist metaphosphoric acid, both of which leave much to be desired as lubricants for high vacuum work. The former tends to leak and to "freeze," while the latter "freezes" unless the stopcocks are turned very frequently.

During attempts to develop a more satisfactory lubricant for use in work at present in progress, the writer discovered that a thick, sirupy liquid with practically no tendency to crystallize on standing could be obtained by preparing a solution of the three phosphoric acids in one another. This mixture may be prepared with almost any desired viscosity by simply varying the proportions of the components. Due to the hygroscopic nature of the material, it must, of course, be protected from moisture but this can easily be done by using mercury seal stopcocks. Absorption of water causes crystallization to take place, with a simultaneous thinning of the remaining liquid phase.

It must be admitted that this mixture is not as satisfactory a lubricant as grease, and stopcocks on standing under vacuum tend to "freeze" to a certain extent. However, they can be loosened very readily by warming gently with a flame. This latter operation should be performed, if possible, when the system is not evacuated but can be performed under vacuum, if necessary. In the latter case the tendency to "freeze" is increased but in the former it is not.

Due to this slight tendency to "freeze" the stopcocks, it is advisable to re-grind the latter with fine emery powder before using with the phosphoric acid lubricant. If one takes the additional precaution of finishing with rouge, "freezing" will be reduced to a minimum.

For high vacuum work the following directions will yield a mixture that has been found by the writer to be very satiefactory. On heating the mixture of ortho- and metaphosphoric acids above the decomposition point of the former, there will also be formed some pyro acid. This increases the complexity of the mixture and probably hinders crystallization.

Directions.—Add 18 g. of metaphosphoric acid to 35 g. of 85% orthophosphoric acid, containing a drop or two of concentrated nitric acid, to destroy reducing substances. Heat to 300° in a platinum crucible, over a period of fifteen minutes, then hold at 300° for. fifteen minutes. Cool to about 100° and transfer equal portions to three or four small bottles equipped with rubber stoppers. (Division into three or four portions is recommended because the lubricant is usually spoiled by the admission of moist air into the bottle before it is nearly all used.)

CONTRIBUTION FROM THE
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H. N. STEPHENS

RECEIVED JULY 6, 1929
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A New Regulator Allowing Rapid Changes in the Temperature Setting **of** the Thermostat.—In the course of an investigation involving the use of a thermostat at widely different temperatures, the author has designed a vapor-pressure regulator that made possible rapid changes from one temperature setting to another. Although many forms of vapor-pressure regulators have been used before, it is believed that certain new features in the construction and operation of the device justify a detailed description of it.

The filling of the apparatus is carried out by a suitable application of vacuum and tilting. When ready for operation, it has both ends sealed. The bulb (Fig. 1) contains a vapor phase devoid of air, a suitable liquid and a layer of mercury. The space in the inclined tube above the mercury is evacuated. The whole rests on an iron bar (not shown in the figure) bent to fit the tube and capable of rotation around an axis at O.

As the thermostat is heated, the mercury level in the tube rises. When the desired temperature is reached, the upper wire from the relay is attached to the nearest electrode (tungsten wire sealed into the pyrex glass), and the apparatus is tilted to just make or break contact. After this the regulator will work for weeks without requiring any attention.

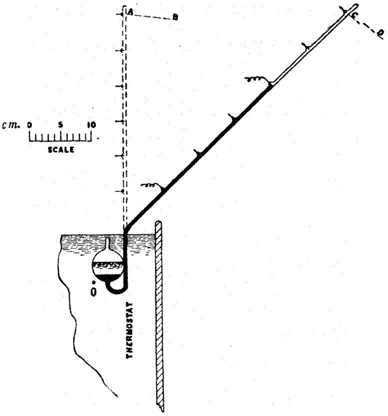

Fig. 1.

Using aniline as the source of vapor pressure, the author was able to obtain any temperature within the range 110 to 160" by using the proper electrode. The temperature was kept constant to within 0.1".

It will be noticed that the tube is bent through an angle of about 45°. With the apparatus fixed, to every electrode there corresponds a certain temperature. Intermediate values are obtained by tilting, at which time all points move along inclined arcs CO. Were the tube made vertical, the points of contact would move along nearly horizontal arcs AB, necessitating much larger angles of rotation for the same temperature shift. Incidentally, the sensitiveness of the regulator is increased by a factor of about 1.4.

The chief advantage of this apparatus lies in the ease with which the thermostat temperature setting can be changed. Furthermore, contact is made in a sealed tube, with no air present, thus eliminating any possibility of contamination.

Contribution from the
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

A METHOD OF DETERMINING THE ARSENIC CONTENT OF ORGANIC ARSENICALS

BY F. E. CISLAK[1] AND CLIFF S. HAMILTON

RECEIVED MARCH 7, 1929 PUBLISHED FEBRUARY 6, 1930

Numerous methods have been proposed for the estimation of the arsenic content of organic compounds containing arsenic. Bunsen[2] estimated the arsenic content by difference; Dumas[3] determined the increase in weight of the combustion tube after the elementary analysis of the organic arsenical and ascribed this increase to the presence of arsenious oxide. In other procedures[4] the compound was oxidized by fusion and the arsenic weighed as magnesium pyroarsenate. Monthulé[5] destroyed the organic matter present by nitric acid. The work of F. A. Norton and A. E. Koch[6] gave rise to numerous volumetric methods. Among the most widely known of these methods may be mentioned those of Lehmann,[7] Ewins[8] and Robertson.[9]

In all the above volumetric methods a standard iodine solution is used as the titrating solution with starch as an indicator. Rather exacting conditions are required in order to get reliable and reproducible results by these methods.[10]

A means of determining arsenic in inorganic compounds by the potentiometric method has been proposed by Zintl and Wattenberg.[11] The authors adapted this method to the determination of the arsenic content of organic compounds. The method is described below.

Details of Method

A saturated calomel electrode was used as the cathode, and a piece of platinum

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[1] Research Fellow under a grant from Parke, Davis and Company. This article is an abstract of a portion of a thesis submitted to the Graduate School of Northwestern University by F. E. Cislak in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Bunsen, *Ann.*, **24, 278 (1837).**

[3] Dumas, *ibid.*, **27, 149 (1838).**

[4] La Coste and Michaelis, *ibid.*, **201, 224 (1889);** Pringsheim, *Am. Chem.* **J.**, *31*, 386 **(1904).**

[5] Monthulé, *Ann. chim. anal.*, *9*, **308 (1904).**

[6] Norton and Koch, THIS JOURNAL, **27, 1249 (1905).**

[7] Lehmann, *Apoth.* **Ztg., 27, 545 (1912).**

[8] Ewins, **J.** ***Chem. Soc.***, *109*, **1355 (1916).**

[9] Robertson, THIS JOURNAL, **43, 182 (1921).**

[10] Since the completion of the work described in this article a method of estimating the arsenic content of organic compounds with the aid of a standard bromate solution and the use of suitable indicators has been published by Schulek and Villecz, Z. *anal. Chem.*, **76, 81 (1929).**

[11] Zintl and Wattenberg, *Ber.*, 56, **472 (1923).**

wire sealed into a T-tube served as the anode; these electrodes were connected directly to a Leeds and Northrup portable potentiometer. A slow stream of carbon dioxide was passed through the anode above (not into) the solution. A mechanical stirrer was provided. An approximately 0.05 *N* solution of potassium bromate was used as the titrating solution.

Procedure.—Between fifteen hundredths and two-tenths of a gram of the substance was weighed out and introduced into a Kjeldahl flask of 300-cc. capacity. Twenty grams of potassium sulfate, 0.2 to 0.3 g. of starch, and 20 cc. of concentrated sulfuric acid were then added to the sample in the flask and the mixture was warmed gently over a small flame for about thirty minutes; then the size of the flame was increased very slightly and the heating continued for another thirty minutes, when the flame was increased to a fairly good size and the digestion continued until the solution became clear and colorless.[12] The flask was removed as soon as the solution became colorless, allowed to cool to about 80° and diluted with approximately 70 cc. of distilled water. The solution was transferred quantitatively into a beaker of 600-cc. capacity and to this solution 30 cc. of concentrated sulfuric acid was added and sufficient water to make the total volume of the solution about 400 cc. The solution was then ready for titration.

The arm of the calomel half-cell was rinsed with distilled water and then about 10 cc. of the potassium chloride solution from the reservoir was run through the cell. The platinum wire was also rinsed with water. The two electrodes were then immersed in the solution which was to be titrated and connected to the potentiometer. A slow stream of carbon dioxide was turned on and the stirrer started.

The resistance of the potentiometer was adjusted so that there was no deflection of the galvanometer when this instrument was thrown into the circuit. The bromate solution was then added slowly from a buret. At this stage of the titration the solution was added at the rate of about 4 cc. per minute.[13] After the addition of each cubic centimeter of the standard solution the galvanometer was thrown into the circuit and the deflection of the galvanometer needle observed. The deflection, at this point, was so slight that by merely increasing the resistance a very small amount, corresponding to one to two hundredths of a volt, the null point was again reached. When the end-point was only about 2 cc. away,[14] the rate of addition was slowed down to such an extent that it was possible to observe the deflection of the galvanometer needle after the addition of each drop. When the end-pint was reached, one drop of the bromate solution caused a rather complete deflection of the galvanometer needle. This single drop threw the needle to one side so strongly that resistance

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[12] The heating should not be prolonged after the solution has cleared as there is a tendency for the hot sulfuric acid, in the absence of any other reducing matter, to oxidize the trivalent arsenic.

[13] The addition of the bromate solution should not be too rapid as the reaction is not extremely fast in reaching equilibrium even in the presence of so high an acid concentration.

[14] In this method of determining the end-point of the reaction, there is no indication of an approach to it. Hence, in order not to go past the end-point, one must either add the reagent very slowly during the entire course of the titration or else have an idea as to the amount of reagent the given sample will require.

corresponding to at least 0.200–0.400 volt was **necessary** to balance the circuit.[15]

Experimental

A large number of organic arsenicals was analyzed by the method herein described; the results of a few of these analyses are given in Table I.

TABLE I

TESTS OF THE METHOD

Compound	Arsenic trioxide		Arsanilic acid		*n*-Butylarsonic acid		Diphenylamine-*o*-arsonic acid	
Sample, g.	0.1002	0.1013	0.2022	0.2009	0.1986	0.1987	0.2095	0.2199
As found, %	75.76	75.78	34.59	34.58	41.26	41.24	25.62	25.54
As calcd., %	75.75	75.75	34.56	34.56	41.21	41.21	25.57	25.57
Deviation, %	+0.01	+0.03	t0.03	+0.02	+0.05	+0.03	+0.05	−0.03

Summary

The arsenic content of organic compounds can be determined readily and accurately by digesting the compound with hot sulfuric acid in the presence of potassium acid sulfate, diluting the solution thus obtained and titrating electrometrically with potassium bromate.

EVANSTON, ILLINOIS

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

THE CATALYTIC "COUPLING" OF MANGANESE DIOXIDE WITH PHOSPHORIC OR SULFURIC ACID AS AN OXIDIZING AGENT. THE EFFECT OF ACIDITY ON THE OXIDATION OF BUTYRIC ACID WITH HYDROGEN PEROXIDE

BY EDGAR J. WITZEMANN

RECEIVED MAY 13, 1929 PUBLISHED FEBRUARY 6, 1930

The results given in this paper constitute a part of a study of the influence of a few chemical variables upon the oxidation of butyric acid.[1] This report concerns the influence of the amount and nature of the acids present on the oxidation of butyric acid by hydrogen peroxide.

The Influence of Phosphoric Acid.—Since previous work had brought out the catalytic properties of dialkali phosphate in the oxidation of butyric acid, attention was first given to phosphoric acid, in studying the effect of acidity upon this oxidation, especially in view of the fact that it is possible that the catalytic effects of dialkali phosphates may be due to the intermediate formation of a perphosphate.

[15] When this 0.200–0.400 volt increase in e.m.f. caused by a single drop of the bromate solution is compared to the increase of 0.01–0.03 volt caused by one cubic centimeter of the solution, it is obvious that the end-point is extremely easy to recognize.

[1] (a) Witzemann, *J. Biol. Chem.*, **35**, 83 (1918); 49,123 (1921); (b) THIS JOURNAL, 48,202,208,211 (1926); 49,987 (1927).

Experiments were, therefore, set up with free phosphoric acid: 100 cc. of solution contained 50 cc. of 3% hydrogen peroxide, 0.25 g. of butyric acid as the potassium salt and phosphoric acid as indicated below. These experiments were allowed to stand at room temperature for forty-two to forty-five hours before analysis for acetone. The methods of analysis used were those previously described.[2]

	1	2	3	4	5	6	7
H_3PO_4 (85%), g.	0.0	0.066	0.198	0.33	0.66	1.32	3.3
Molarity, M	....	0.0057	0.0171	0.0285	0.057	0.014	0.285
Acetone, g.	0.0011	0.0010	0.0022	0.0034	0.0020	0.0128	0.0588

Calculated acetone yield, 0.164.

In the above experiments, the results of which are typical, an increasing yield of acetone was associated with increasing acidity.

The use of manganese dioxide during distillation had been adopted as a routine procedure in oxidations with hydrogen peroxide in order to obtain distillates free from hydrogen peroxide. It had become customary to add about **3** to 4 g. of manganese dioxide for this purpose. Such high yields of acetone as those indicated in (6) and (7) were obtained when no more than this was used. Under these conditions the mixture in the distilling flask becomes gray in (6) and (7) before distillation is complete and the mixture foams freely throughout the distillation. If a large excess of manganese dioxide is added the mixture remains black, tends to bump during distillation and no more acetone is obtained than in (4) and (5).

Data Concerning the Phosphoric Acid–Manganese Dioxide Catalysis.—The facts that the manganese dioxide was reduced with the formation of manganese phosphate and that the addition of large excess of manganese dioxide led to a striking decrease in the yield of acetone, suggested that manganese dioxide is vitally concerned in this process. Special test experiments brought out the following facts. When phosphoric acid and manganese dioxide but no hydrogen peroxide were allowed to act upon potassium butyrate as usual, no acetone whatever was obtained. Although it is generally stated that dilute sulfuric acid does not liberate oxygen from manganese dioxide, a suitably arranged test experiment was made with this acid as well as with phosphoric acid. No oxygen was evolved in the course of a week. When phosphoric acid and hydrogen peroxide were used with potassium butyrate and the peroxide was decomposed by making the solution alkaline and adding precipitated calcium carbonate, very little acetone was obtained. Moreover, the hydrogen peroxide concentration remained unchanged in the experiments containing phosphoric acid, butyric acid and peroxide, for as long as three weeks, as was shown by permanganate titrations.

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[2] Witzemann, *J. Biol. Chem.*, 49, 123 (1921).

These and other test experiments developed the fact that this catalysis is dependent upon the presence of two components and that both the hydrogen peroxide and the manganese dioxide are reduced when the best results are obtained.

The only well-known reaction in which an acid interacting with manganese dioxide causes the decomposition of hydrogen peroxide with the reduction of the manganese dioxide is the following

$$H_2SO_4 + MnO_2 + H_2O_2 \longrightarrow MnSO_4 + 2H_2O + O_2$$

Nothing could be found in the literature concerning oxidations brought about by this system.

Test experiments showed that sulfuric acid may be replaced with phosphoric acid. Small concentrations of phosphoric acid were used (comparable with those in Nos. 5, 6 and 7 above) with a considerable excess of manganese dioxide. It was noted that the presence of the phosphoric acid very materially retarded the time rate of oxygen evolution upon addition of manganese dioxide. The volume of oxygen evolved was measured in each case. The results showed that at the lower concentrations all of the phosphoric acid reacted apparently as follows

$$2H_3PO_4 + 3MnO_2 + 3H_2O_2 \longrightarrow Mn_3(PO_4)_2 + 6H_2O + 3O_2 \qquad (1)$$

The excess hydrogen peroxide not required for this reaction was decomposed thus

$$MnO_2 + 2H_2O_2 \longrightarrow MnO_2 + 2H_2O + O_2 \qquad (2)$$

In any case the observed volume of oxygen corresponded closely with the volume calculated on this assumption. With higher concentrations of phosphoric acid not all of the phosphoric acid entered reaction according to (1) and so the observed volume of oxygen was less than that calculated on this assumption. This suggests that at the lower concentrations all of the phosphoric acid enters into some complex relation with hydrogen peroxide before the reaction is over.

These experiments furnish a clew for the interpretation of the catalytic oxidations of butyric acid described below.

The Influence of Sulfuric and Boric Acids on Butyric Acid Oxidation.—Having learned that phosphoric acid interacts like sulfuric acid with manganese dioxide and hydrogen peroxide, it was of interest to learn how sulfuric acid influences the oxidation of butyric acid. Flasks containing 100 cc. of solution of which 50 cc. was 3% hydrogen peroxide and 0.25 g. butyric acid, containing also sulfuric acid as indicated below, were otherwise treated as in the phosphoric acid experiments and upon analysis the contents gave the results shown

Sulfuric acid, g.	0.28	0.56	1.12	2.80
Molarity of acid, M	0.03	0.06	0.11	0.28
Acetone yield, g.	0.0036	0.0053	0.0052	0.0053

Such negative results were obtained several times until suddenly data similar to those given below were obtained by changing the conditions slightly in some way.

An experiment like the last of this group was set up containing 500 cc. of 0.28 *M* sulfuric acid, 500 cc. of **3%** hydrogen peroxide, 2.50 g. of butyric acid in 50 cc. of water and 1.59 g. of potassium hydroxide in 50 cc. of water. After standing for forty-five hours the mixture was distilled in portions of 110 cc. with 50 cc. of distilled water using various catalysts for the decomposition of the peroxide.

(a) and (b) Added 3 to 4 g. of manganese dioxide (Baker's analyzed) and distilled slowly. Acetone found, 0.0514 g. (31.3% of the possible yield) and 0.0552 g., respectively.

(c) Repeated (a) with a much less dense form of manganese dioxide and found 0.0464 g of acetone.

(d) Repeated (a) with three times as much managnese dioxide. The evolution of oxygen was more rapid and only 0.0036 g. of acetone was found.

(e) Added a teasponful of unglazed porcelain chips and distilled as slowly as possible. Hydrogen peroxide was not present in the distillate and 0.0335 g. of acetone was found.

(f) Added a teaspoonful of 60-mesh quartz sand and distilled slowly as in (e). Acetone found, 0.0340 g.

These results show that the influence of sulfuric acid on this oxidation is at least roughly similar to that of phosphoric acid.

Boric Acid.—Boric acid was selected for some additional experiments because in some respects it is so different from either of the two acids previously used. The reaction mixture was made up as follows: 250 cc. of 0.28 M boric acid, 250 cc. of **3%** hydrogen peroxide, **1.25** g. of butyric acid in 25 cc. of water and 0.80 g. of potassium hydroxide in 25 cc. of water.

(a) After standing for two days at room temperature, 110 cc. of the above with 50 cc. of water was distilled slowly with about 2 g. of manganese dioxide. The manganese dioxide was not visibly changed and no peroxide distilled over. The acetone obtained was 0.0029 g. or 1.7% of the possible yield.

(b) The preceding distillation was repeated with 1 g. of manganese dioxide with slow heating in the beginning. The results were the same--0.0031 g. of acetone.

(c) When (a) was repeated using a teaspoonful of unglazed porcelain chips and no manganese dioxide, 0.0823 g. of acetone or a 50.2% yield was obtained. A repetition gave 0.01023 g. of acetone or a 62.3% yield.

The hydrogen peroxide content of the solution was practically unchanged after standing for a month in the laboratory.

It seemed that manganese dioxide must necessarily catalyze this oxidation as well as porcelain chips, but a good many trials failed to give the desired result.

The Fate of the Butyric Acid Used in These Oxidations.—The preceding data suggest that a considerable portion of the butyric acid is oxidized in these experiments. Some more definite data were desired.

The oxidation mixture with phosphoric acid was set up as follows:

250 cc. of 0.285 *M* phosphoric acid, 250 cc. of 3% hydrogen peroxide, 1.25 g. of butyric acid in 25 cc. of water and 0.8 g. of potassium hydroxide in 25 cc. of water. The hydrogen peroxide content of this solution was 1.36%, as determined by titration with potassium permanganate; after standing at room temperature for about three weeks it was unchanged.

Two hundred and twenty cc. of the mixture with 50 cc. of water and 3 to 4 g. of manganese dioxide were distilled slowly. The distillate was made up to 300 cc.; 125 cc. of this analyzed for acetone gave 0.147 g. of acetone for the entire distillate, a yield of 44.8%.

A portion of 110 cc. with 50 cc. of water and 2 g. of manganese dioxide was treated similarly. The distillate was made up to 225 cc. and fractionated in four 50-cc. portions, which neutralized 0.1 N alkali as follows: (1) 10 cc., (2) 6.4 cc., (3) 5.07 cc., (4) 3.13 cc., (residue) 1.87 cc., total 26.47 cc. This result indicated that considerable unchanged butyric acid was present.[3] These solutions were united, acidified with phosphoric acid and again distilled. The distillate was made up to 240 cc.; 120 cc. was then distilled off. This neutralized 16.53 cc. of 0.1 N alkali. The residue in the flask required 8.8 cc. of alkali.

In order to determine approximately how much butyric and acetic acid was present, it was desired to use the method of Wiegner and Magasanik[4] as applied by Virtanen.[5] In order to do this effectively the distillation constants for very dilute solutions of these acids were determined in our own apparatus. It was found that when 240 cc. of dilute acid (equivalent to 15 to 25 cc. of 0.1 N sodium hydroxide) was distilled, the first 120 cc. of distillate when acetic acid was used required 36.0% of the total alkali, while with butyric acid it required 71.6%. These figures are slightly lower than those given by Virtanen for the apparatus used by him.

Using the above data we have the following simultaneous equations

$$\begin{matrix} A + B = 25.33 \\ 0.360\,A + 0.716\,B = 16.53 \end{matrix} \quad \left\{ \begin{matrix} \text{A and B are the alkali equivalents of acetic} \\ \text{and butyric acids, respectively.} \end{matrix} \right.$$

Solving for A and B we obtain A = 4.49 cc., B = 20.84 cc.; *i. e.*, 74.4% of the butyric acid was recovered unchanged in this experiment.

Virtanen reports that this method serves also as a criterion of the purity of the substances used. In order to check the qualitative nature of the mixture being analyzed, a synthetic mixture of pure acetic and butyric acids was prepared in 240 cc. of water having the supposed composition of the unknown. The half distillate neutralized 16.80 cc. of 0.1 N alkali, while the residue required 8.85 cc. The total acidity, therefore, corresponded to 25.65 cc. of 0.1 N alkali. When these data were calculated

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[3] Witzemann, THIS JOURNAL, 41, 1946 (1919).

[4] Magasanik, *Chem.-Ztg.*, 43, 656 (1919); *Analyst*, 45, 24 (1920); *C. A.* 14, 1947 (1920).

[5] Virtanen, *Soc. Scient. Fennicae, Comm. Phys. Math.*, 1, No. 36 (1923); see also THIS JOURNAL, 50, 3138 (1928).

by the above equations, the acetic acid found neutralized 4.38 cc. of 0.1 N alkali, while the butyric acid neutralized 21.27 cc. This corresponds very nearly to the amounts added and gives good agreement with the data for the unknown mixture.

A simultaneous determination of acetone and carbon dioxide was made using a method previously described;[2] 110 cc. of the original mixture with 50 cc. of water and 1 g. of manganese dioxide and a few porcelain chips were heated slowly in the apparatus: 0.0657 g. of acetone or 40.1% and 0.155 g. of carbon dioxide or 31.0% were obtained. One-fifth of the distillate diluted to 100 cc. was treated with silver oxide (from 5 g. of silver nitrate) and 4 cc. of concentrated ammonium hydroxide in a sealed magnesium citrate bottle in a warm water-bath for about four hours.[6] On filtering off the silver residues, acidifying with hydrochloric acid and distilling, 0.0456 g. or 27.8% of acetone was obtained. Quite *a* little silver chloride was precipitated, indicating that a corresponding amount of acid formation had occurred.

When the above and other results not given are summarized, a fairly good account can be rendered of the butyric acid used in spite of the general variations in the results of the oxidation. Forty per cent. or more of the butyric acid used was recovered unchanged; as much as 28% was oxidized to acetone and carbon dioxide; enough more carbon dioxide was formed to account completely for **23%** of the butyric acid; quite a little acetic acid was also found.

With Sulfuric Acid.—The oxidation mixture was set up as follows: 500 cc. of 0.28 M sulfuric acid, 500 cc. of hydrogen peroxide, 2.5 g. of butyric acid in 50 cc. of water and 1.59 g. of potassium hydroxide in 50 cc. of water. The peroxide titer remained unchanged three days later.

Aliquot portions of this solution were analyzed by the methods used above. On the basis of the butyric acid originally present, this solution yielded 0.139 to 0.20 g. of acetone, *i. e.*, a minimum of 42.1%. Fractionation and analysis of the volatile acids present showed that about 23.7% of the butyric acid was recovered unchanged, while the remainder of the volatile acid was apparently pure acetic acid, as shown by fractionation of controls having the same acid titer and presumably the same composition. In some analyses smaller amounts of volatile acids were obtained, but unchanged butyric acid was always present.

The acetone as determined in the crude distillate varied from **35** to 60%, but in the former case dropped to 23.8% after treatment with silver oxide and ammonia.

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[6] Portions of a solution containing about 0.05 g. of pure acetone in 50 cc. were treated with silver oxide, etc., at the same time. These solutions showed 0.045 g. of acetone upon analysis, whereas the untreated solution gave 0.046 g. of acetone. This showed that acetone is not materially influenced by this treatment.

From 28.8 to 44.3% of the carbon in the butyric acid was converted into carbon dioxide, which was recovered as barium carbonate.

The results obtained with sulfuric acid correspond to those obtained with phosphoric acid, except that very small amounts of unchanged butyric acid are recovered. The transformation is much more profound in this case. More undetermined products are formed, and the results do not so adequately account for the butyric acid used as was the case with phosphoric acid.

Summary

The influence of the presence of considerable amounts of free acids (phosphoric, sulfuric and boric) upon the oxidation of butyric acid with hydrogen peroxide was studied. Under these conditions the concentration of hydrogen peroxide remains unchanged indefinitely and no oxidation occurs unless or until a suitable catalyst is added. The catalyst most frequently used was manganese dioxide. It is thought that the oxidation observed arose from the action of this compound upon the peroxide compound of the acid, although this point was not proved. Under these conditions the butyric acid present is often largely oxidized, with the formation of much acetone, carbon dioxide and acetic acid. The volatile acid products consisted of acetic acid and unchanged butyric acid.

No adequate interpretation of this unexpected catalytic system was developed.

This catalytic oxidation of butyric acid, unlike that brought about by ammonia and sodium phosphate, is a very rapid reaction.[1b,2]

MADISON, WISCONSIN

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

THE ACTION OF BROMINE ON PHENOLPHTHALEIN. FURTHER EVIDENCE OF THE TAUTOMERIC CHARACTER OF PHENOLPHTHALEIN

BY ALLAN R. DAY

RECEIVED JUNE 28, 1929 PUBLISHED FEBRUARY 6, 1930

It was noted during the course of previous work[1] that the action of bromine (as generated by acidifying a bromate–bromide mixture) on phenolphthalein varied greatly with conditions. In the presence of a solvent such as chloroform tetrabromophenolphthalein was always formed. This, of course, is the usual and well-known reaction. The lack of color of this derivative indicates its lactoid structure. An attempt was made to make this bromination the basis of a quantitative determination but the results obtained varied from the theoretical by 1 to 2%.

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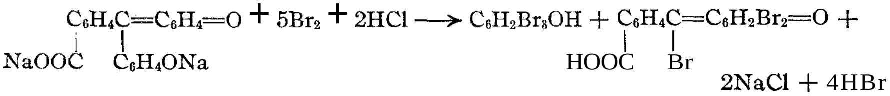
[1] **Day** and Taggart, *Ind. Eng. Chem.*, **20**, **545** (1928).

When the phenolphthalein was dissolved in sodium hydroxide and the resulting solution acidified with hydrochloric acid, in the presence of an excess of bromate and bromide, a brownish-yellow precipitate was formed. It was found, by adding potassium iodide and titrating the liberated iodine with thiosulfate, that the formation of the brownish-yellow precipitate was accompanied by the loss of five molecules of bromine. The directive groups present in the original molecule seemed to eliminate the possibility that the fifth bromine molecule reacted by substitution. The brownish-yellow color of the precipitate indicated the possible presence of a quinoid structure. It was with the hope that a study of this reaction would furnish more evidence of the chromoisomerism of phenolphthalein that this investigation was undertaken.

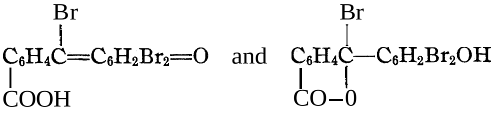
The brownish-yellow material on being carefully heated yielded a sublimate of long, colorless needles and finally a brownish residue remained from which no further sublimate could be obtained. The sublimate consisted entirely of tribromophenol. (Baeyer noted[2] that when dry phenolphthalein was rubbed together with an excess of bromine, tribromophenol was obtained as one of the products. Baeyer, however, did not investigate the reaction.) Further investigation showed that for every molecule of phenolphthalein brominated, one molecule of tribromophenol split off. On the basis of this evidence the following reaction was assumed to take place



$$\underset{\substack{|\\ NaOOC}}{C_6H_4}\underset{\substack{|\\ C_6H_4ONa}}{C}{=}C_6H_4{=}O + 5Br_2 + 2HCl \longrightarrow C_6H_2Br_3OH + \underset{\substack{|\\ HOOC}}{C_6H_4}\underset{\substack{|\\ Br}}{C}{=}C_6H_2Br_2{=}O + 2NaCl + 4HBr$$

Such a reaction is not an unusual one as many cases are known in which a substituent ortho or para to an OH group is readily replaced by bromine, for example, o- and *p*-hydroxybenzoic acids yield tribromophenol.

The quinoid compound, illustrated above, should be capable of existing in two forms



$$\underset{\substack{|\\ COOH}}{C_6H_4}\overset{\substack{Br\\ |}}{C}{=}C_6H_2Br_2{=}O \quad \text{and} \quad \underset{\substack{|\\ CO-}}{C_6H_4}\overset{\substack{Br\\ |}}{\underset{\substack{|\\ O}}{C}}{-}C_6H_2Br_2OH$$

Colored Colorless

This was found to be the case. After dissolving the colored form in alcohol, it was recovered, by very slow evaporation, only in the colorless or lactone form. The bromine content of both forms proved to be somewhat less than the theoretical, due to incomplete bromination. An attempt was made to overcome this difficulty by dissolving the yellow form in sodium hydroxide and acidifying the solution with hydrochloric acid in the presence of bromate and bromide. The precipitate obtained,

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[2] Baeyer, *Ann.*, **202**, 78 (1880).

however, was not what was expected. It was reddish-brown in color and its bromine content had increased about 15%. It is hoped, in later work, to be able to prepare these compounds by different methods and conclusively prove the structure of the quinoid and lactone forms.

Tetrabromophenolphthalein when brominated under similar conditions yielded the same products. It is probable that tetrabromophenolphthalein is an intermediate product in the reaction under investigation.

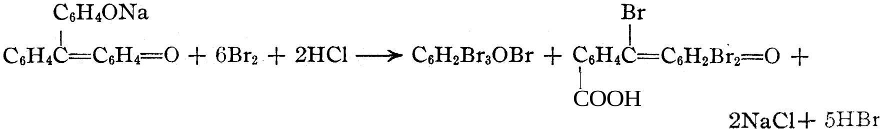
Experimental Part

Bromination of **Phenolphthalein.**—Five grams of phenolphthalein was dissolved in a little more than the calculated amount of 3 N sodium hydroxide. To this was added a solution containing 5 g. of potassium bromate and 18 g. of potassium bromide and the resulting solution was then diluted to one liter. The solution was then vigorously shaken or stirred and 15–20 cc. of 12 N hydrochloric acid slowly added. The precipitate at first was very voluminous but after shaking for ten to thirty minutes it settled very nicely and was easily filtered. The brownish-yellow precipitate was dried between filter paper. The precipitate on drying becomes coated with tiny colorless needles of tribromophenol and a small amount of bromine is given off, the latter probably being due to the decomposition of $C_6H_2Br_3OBr$ to $C_6H_2Br_3OH$.

Identification of Sublimate.—The sublimate was obtained, by carefully heating (50–75") the dried precipitate from above, in the form of long colorless needles. The sublimate melted at 92°. The bromine content determined by a sodium peroxide fusion method was 72.39%. These results check very well the melting point and bromine content of tribromophenol, 92° and 72.48%.

In two other cases the brownish-yellow precipitate, as first obtained, was suspended in water and treated with sulfur dioxide to reduce the $C_6H_2Br_3OBr$ to $C_6H_2Br_3OH$. The dried precipitate from this treatment was subjected to careful sublimation. The sublimate melted at 92° and the bromine content was 72.30%.

Determination of the Total Bromine Consumed in the Reaction.—Half a gram of phenolphthalein was dissolved in a slight excess (1–2 cc. in excess) of 3 N sodium hydroxide and the resulting solution diluted to 250 cc. A 25-cc. aliquot was pipetted into a 500-cc. iodine flask, followed by 25 cc. of 0.2 N bromine solution (75 g. of potassium bromide and 5.6 g. of potassium bromate per liter). Five cc. of 12 N hydrochloric acid was added and the flask stoppered at once. It was vigorously shaken and allowed to stand for one hour with occasional agitation. The flask was then cooled and 5 cc. of 40% potassium iodide solution introduced. After vigorous shaking the liberated iodine was titrated with 0.1 N thiosulfate solution. The results from a series of analyses, based on a bromine equivalent of $5Br_2$, varied from 98 to 99.5%. The essential equations for the reaction may be represented as follows



$$C_6H_4\overset{\displaystyle C_6H_4ONa}{\overset{|}{C}}{=}C_6H_4{=}O + 6Br_2 + 2HCl \longrightarrow C_6H_2Br_3OBr + \underset{\displaystyle COOH}{\underset{|}{C_6H_4}}\overset{\displaystyle Br}{\overset{|}{C}}{=}C_6H_2Br_2{=}O + 2NaCl + 5HBr$$

$$C_6H_2Br_3OBr + 2HI \longrightarrow C_6H_2Br_3OH + I_2 + HBr$$

Estimation of Tribromophenol Formed.—The tribromophenol was determined by weighing the sublimate obtained from the bromination of a known amount of phenolphthalein. The results in all cases indicated the formation of one molecule of tribromophenol for one molecule of phenolphthalein. It was found necessary to repeat the bromination in order to complete the reaction. For example, 1.1283 g. of phenolphthalein was brominated as usual. The precipitate was next suspended in water and treated with sulfur dioxide. The dried precipitate was then subjected to careful sublimation. When sublimation had ceased, the residue was again dissolved in sodium hydroxide and the bromination repeated. In this particular case three brominations followed by sublimation were necessary before no more sublimate was formed. The 1.1283 g. of phenolphthalein yielded 1.1629 g. of tribromophenol; theoretical, 1.1736 g.

Analysis of the Quinoid Form.—The brownish-yellow precipitate as first formed was dried, washed with ether and finally heated carefully until sublimation had completely stopped. The bromine content of the residue varied from 48 to 51.08%; theoretical, 51.80%. The low results were undoubtedly due to incomplete bromination. This was demonstrated in the previous paragraph. All attempts to rebrominate the product have failed, as some other reaction (perhaps further substitution or oxidation) resulted. The substance melted at 229–236° with decomposition. It dissolved in sodium hydroxide, forming a greenish-yellow solution which finally became yellow.

Analysis of the Colorless or Lactone Form.—The yellow form, purified as above, was shaken with a large volume of absolute alcohol. It dissolved very slowly, forming a yellow solution which quickly became colorless. When this solution was evaporated almost to dryness, a colorless apparently crystalline material was obtained. This material, after drying, melted at 270–273° with some decomposition. The bromine content checked very well with that of the yellow form. For example, the bromine content of one sample of the yellow was found to be 49.62%. A portion was then changed to the colorless form and the bromine content was now found to be 49.75%. The colorless form dissolved in sodium hydroxide to form a colorless solution. A slight violet color appeared at first but quickly disappeared. Whether this trace of color was due to the lactone form or to the presence of a trace of tetrabromophenolphthalein cannot be answered at present.

Discussion

Friedländer,[3] in 1893, assigned a quinone structure to phenolphthalein salts. About the same time Meyer and Spengler proved it to be a dibasic acid. The tautomeric character of phenolphthalein has been demonstrated since then by various workers, including Stieglitz,[4] Acree and Slagle,[5] Green and King,[6] Hantzsch and Meyer,[7] Meyer and Marx,[8] Orndorff, Gibbs and McNulty,[9] and Gibbs and Shapiro.[10] It was shown by some of these investigators that esters could be prepared from phenolphthalein. They showed that the labile quinoid modifications were yellow or orange, but rearranged in the process of crystallization to give the colorless, stable lactoid form.

According to the views expressed by these papers, the appearance of color during the process of salt formation, with phenolphthalein, would indicate that the color change depends upon changes in constitution rather

[3] Friedlander, *Ber.*, 26, 172 (1893).

[4] Stieglitz, THIS JOURNAL, 25, 1112 (1903).

[5] Acree and Slagle, *Am. Chem.* J., 42, 115 (1909).

[6] Green and King, *Ber.*, 39, 2365 (1906).

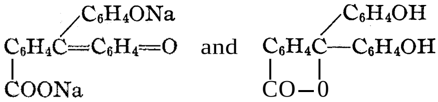
[7] Hantzsch and Meyer, *ibid.*, 40, 3480 (1907).

[8] Meyer and Marx, ibid., 40, 1437 (1907).

[9] Orndorff, Gibbs and McNulty, THIS JOURNAL, 48, 1994 (1926).

[10] Gibbs and Shapiro, *ibid*, 50, 2978 (1928); Proc. *Nat.* Acad. *Sci.*, 14, 251 (1928).

than upon the formation of ions. Any ions which may form can possess color only if the non-ionized molecules from which they come are colored. The sodium salt is assumed to have a quinoid structure, while free phenolphthalein has a lactone structure



$$\begin{array}{l} \quad\diagup C_6H_4ONa \\ C_6H_4C{=}C_6H_4{=}O \\ | \\ COONa \end{array} \quad \text{and} \quad \begin{array}{l} \quad\diagup C_6H_4OH \\ C_6H_4C{-}C_6H_4OH \\ |\quad\ | \\ CO{-}O \end{array}$$

The results presented in this paper can only be explained on the basis of a quinone structure for phenolphthalein in alkaline solution. It is evident that the phenolphthalein must have been brominated before it could change to the lactone structure. If this were not the case, one would naturally expect bromination to proceed as usual with the formation of tetrabromophenolphthalein. That the yellow precipitate first formed is similar to the quinone structure for phenolphthalein is shown by the readiness with which it changes to the colorless or lactone form. The lactone form may be regarded as a derivative of phthalide and the yellow form as the corresponding labile or quinoid structure.

Attempts to prepare these compounds in pure form have not been successful, but it is hoped that later work will overcome some of the difficulties.

Summary

1. It has been shown that the action of bromine (as generated by acidifying bromate–bromide mixtures) upon phenolphthalein varies greatly with conditions. In the absence of a special solvent such as alcohol, chloroform, etc., tetrabromophenolphthalein is not formed. The reaction is accompanied by the loss of five molecules of bromine. Four molecules react by substitution and one by addition.

2. It has been pointed out that the interpretation of the reactions offers further evidence that phenolphthalein possesses a quinoid structure in alkaline solution.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE SYNTHESIS OF BETA-BROMO-ALKYL ETHERS AND THEIR USE IN FURTHER SYNTHESES[1,2]

BY LLOYD C. SWALLEN AND CECIL E. BOORD

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Introduction

The remarkable difference in the reactivity of halogen when substituted in the alpha- or beta-position of an aliphatic ether makes it seem desirable to investigate further these derivatives. The present paper describes the preparation of several β-bromo-alkyl ethyl ethers and their use in further syntheses. An adaptation of the method of Houben and Führer[3] was selected as having the most general application. The synthesis consists of a three-stage process, as indicated by the following reactions

$$CH_3CHO + C_2H_5OH + HCl = CH_3CHClOC_2H_5 + H_2O \quad (1)$$
$$CH_3CHClOC_2H_5 + Br_2 = CH_2BrCHBrOC_2H_5 + HCl \quad (2)$$
$$CH_2BrCHBrOC_2H_5 + RMgBr = CH_2BrCHROC_2H_5 + MgBr_2 \quad (3)$$

The initial step was first described by Wurtz and Frapoli[4] and later improved by Gauthier.[5] The second step consists in the bromination of α-chloro-ethyl ethyl ether. The bromination of this compound has been described by Madinaveitia and Puyal[6] as yielding the α-chloro-β-bromoethyl ether. The present authors do not obtain the same results. Carefully repeated analyses of the product and a study of the yield values show our product to be the dibromo derivative. The final step is an adaptation of the method used by Houben and Führer[3] for the synthesis of β-chloro ethers applied to the preparation of the corresponding bromo derivatives. The yields are good.

The Synthesis of β-Ethoxy-alkyl Mercaptans.[7]—The β-halogenated ethers are remarkable for their lack of chemical reactivity toward some reagents. The β-bromo ethers herein described may be distilled over solid caustic soda without appreciable decomposition. They do, however, react readily with the alkali metal hydrosulfides, forming the corresponding mercaptans. The β-ethoxy-alkyl mercaptans when freshly pre-

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[1] Presented before the Organic Division of the American Chemical Society, in Philadelphia, September 7, 1926.

[2] This paper is abstracted from the Dissertation presented by Lloyd C. Swallen in partial fulfilment of the requirements for the degree of Doctor of Philosophy, to the Faculty of the Graduate School of Ohio State University, June, 1926.

[3] Houben and Führer, *Ber.*, **40, 4993 (1907).**

[4] Wurtz and Frapoli, *Ann.*, **108, 226 (1858).**

[5] Gauthier, *Ann. chim. phys.*, [8] **16, 311 (1909).**

[6] Madinaveitia and Puyal, *Anales soc. españ. fís. quím.*, **16,** 329–337 **(1918).**

[7] While this work was in progress two of the compounds herein described were also prepared by Rojahn and Lemme, *Arch. Pharm.*, **263, 612 (1925).**

pared have a not unpleasant odor closely resembling that of the corresponding chloro ethers. Upon standing they develop the usual mercaptan characteristics as to odor but are quite stable. They are easily converted into the corresponding disulfides and mercaptide chloride derivatives by the usual methods. Ethoxy-ethyl mercaptan readily condenses with acetone to form the corresponding mercaptol and is easily oxidized to ethoxyethylsulfonic acid. The latter compound has been converted into the corresponding sulfochloride and sulfonamide.

β-Bromo Ethers in the Malonic Ester Synthesis.—p-Ethoxy-ethylmalonic ester has been previously described by Byk,[8] who obtained it by the action of β-iodo-ethyl ethyl ether upon malonic ester. It is now shown that an appreciable yield of the same product results even when the β-chloro ether is used. β-Ethoxy-*n*-butyl bromide also reacts readily with malonic ester to form β-ethoxy-*n*-butylmalonic ester in good yield. The latter compound readily yields γ-ethoxy-*n*-caproic acid.

β-Bromo Ethers in the Williamson Reaction.—The β-ethoxyphenetole formed by the action of sodium phenolate upon β-chloro-ethyl ethyl ether is identical in every respect with the product described by Henry[9] as having been derived by the action of sodium alcoholate upon β-chlorophenetole.

Reaction with Aniline.—Cretcher and Pittenger[10] have shown that morpholines are formed by the action of β,β′-dichloro-diethyl ether upon aniline. In an analogous way the monoethoxy-alkylanilines are now produced by the action of aniline upon the β-halogenated alkyl ethyl ethers.

Reaction with Metals.—The most interesting reaction and one which promises to be of great value in synthesis is the decomposition of the β-halogenated ethers in the presence of metals.

Wislicenus[11] observed that β-chloro-acetal reacts with sodium above its melting point to form ethyl vinyl ether as one of the principal products. Wohl and Berthold[12] have also shown that metallic sodium reacts with β-chlorophenetole to form chiefly sodium phenolate and ethylene. Grignard[13] found that β-bromophenetole formed an alkylmagnesium bromide which rapidly decomposed to give phenoxy magnesium bromide and ethylene. In agreement with these facts it is now found that the β-bromo-alkyl ethyl ethers react with magnesium to form olefins as the principal product. In the experimental part of this paper it will be

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[8] Byk, German Patent 285,636; *Chem. Zentr.*, II, 639 (1915).

[9] Henry, Bull. *soc. chim.*, *40*, 324 (1883); *Compt. rend.*, 96, 1233 (1883).

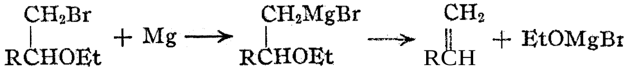
[10] Cretcher and Pittenger, THIS JOURNAL, 47, 163 (1925); Cretcher, Koch and Pittenger, *ibid.*, 47, 1173 (1925).

[11] Wislicenus, *Ann.*, 192, 106 (1878).

[12] Wohl and Berthold, *Ber.*, 43, 2177 (1910).

[13] Grignard, *Compt. rend.*, 138, 1048 (1904).

shown that β-ethoxy-*iso*heptyl bromide reacts with magnesium in the presence of anhydrous ether to yield α-*iso*heptene. The course of the reaction can be easily understood upon the basis of the following mechanism



$$\begin{matrix} CH_2Br \\ | \\ RCHOEt \end{matrix} + Mg \longrightarrow \begin{matrix} CH_2MgBr \\ | \\ RCHOEt \end{matrix} \longrightarrow \begin{matrix} CH_2 \\ \| \\ RCH \end{matrix} + EtOMgBr$$

The significance of this decomposition lies in the fact that the β-bromo-alkyl ethyl ethers may be synthesized readily as indicated above. The yields are good and the reaction seems to be of quite general application. The process promises well as a method for the synthesis of olefins with a definite constitution. The application to the synthesis of olefins has been Further developed and will be offered for publication at an early date.

Experimental Part

Preparation of β-Chloro Ethers.—Several previously described β-chloro ethers were prepared by new or modified methods. The yields and physical constants of these products are shown in Table I.

TABLE I

β-CHLORO ETHERS

Formula	Yield, %	B. p., °C.	d^{20}_{20}
$CH_3—O—CH—CH_2Cl$[14,15]	27	89.5–90.5	1.0659
$C_2H_5—O—CH_2—CH_2Cl$[15,16]	61.7–66	108–109	1.0210
$C_2H_5—O—CHCH_3—CH_2Cl$[17]	54	116–118	0.9798
$C_2H_5—O—CHC_2H_5—CH_2Cl$[17,3]	84	138–139	0.9547
$C_2H_5—O—CHC_6H_5—CH_2Cl$[3]	53	100–105	1.1035

β-Chloro-ethyl methyl ether was prepared by heating a mixture of 80 g. of ethylene chlorohydrin and 120 g. of dimethyl sulfate in a distilling flask over an oil-bath at 145–165° as long as any product distilled. The crude distillate was washed, dried and fractionated.

β-Chloro-ethyl ethyl ether was prepared by dropping slowly a mixture of 175 g. of ethylene chlorohydrin and 350 g. of alcohol into a mixture of 50 cc. of concd. sulfuric acid and 50 cc. of alcohol kept at a temperature of 145–150°. The crude distillate was dried and fractionated using an efficient column, the major portion distilling between 106–110°.

The other three β-chloro ethers of the general type $C_2H_5—O—CHR—CH_2Cl$ were prepared by the method of Houben and Führer. This method consists in adding an ether solution of the appropriate alkylmagnesium bromide to an ether solution of α,β-dichloro-ethyl ethyl ether. Purification was effected in the usual manner.

The Preparation of β-Bromo Ethers.—All attempts to prepare β-bromo ethers by the action of the alkyl hypobromite upon ethylene or of the sodium alcoholate upon ethylene bromide were unsuccessful. A very

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[14] Fileti and Gaspari, *Gazz. chim. ital.*, *27*, II, 293 (1897).

[15] Karvonen, *Ann. acad. sci. Fennicae*, **3A**, 1–103 (1913).

[16] Henry, *Compt. rend.*, 100, 1007 (1885).

[17] Lieben and Bauer, *Ann*, **123**, 130–136 (1862).

satisfactory general method for their preparation was found in an adaptation of the method used by Houben and Fuhrer for the preparation of the β-chloro derivatives. The yield values, analyses and physical constants of six β-bromo ethers prepared by this method are given in Table II.

A. Preparation of a-Chloro-ethyl Ethyl **Ether,**[4,5] $CH_3—CHCl—O—C_2H_5$.—A mixture of 100 g. of paraldehyde and 100 g. of ethyl alcohol was cooled in a freezing mixture and treated with 100 g. of dry hydrogen chloride. The reaction mixture separated into two layers. The upper layer was dried over calcium chloride and fractionally distilled. The portion boiling at 93–96" weighed 162 g., corresponding to a 69% yield. **A** second run using 200 g. of paraldehyde, 210 g. of alcohol and 226 g. of hydrogen chloride yielded 297 g. (64%).

B. Preparation of a,@-Dibromo-ethylEthyl **Ether,**[18] $C_2H_5—O—CHBr—CH_2Br$. Bromination of a-Chloro-ethyl Ethyl Ether.—The a-chloro-ethyl ether, prepared as described above, was cooled in an ice-bath and the theoretical amount of bromine added in small portions. The reaction mixture was allowed to become decolorized or nearly so, after each addition. The reaction proceeded rapidly at first, but quite slowly toward the end. The gas evolved proved to be almost wholly hydrogen chloride. The crude reaction product was submitted **directly** to distillation at diminished pressure. Almost the entire product distilled between 92 and 95° (17 mm.). The yields from two successive runs were 91 and 88.4%. Further fractionation yielded a product boiling at 90–91° (20 mm.); d_{20}^{20} 1.7350.

Anal. Calcd. for $C_4H_8OBr_2$: Br, 68.93. Found: Br, 69.08.

The Bromination Reaction.—The yield and analysis as given above leave no doubt as to the identity of the product as α,β-dibromo-ethyl ethyl ether. These results, however, do not correspond to those obtained by Madinaveitia and Puyal,[6] who have described the bromination product of a-chloro-ethyl ether as the α-chloro-β-bromo derivative. In order to secure additional evidence for the correctness of our conclusions the following experiment[19] was made to determine whether the hydrogen halide was hydrogen chloride.

A portion of a-chloro-ethyl ethyl ether was carefully brominated by the procedure described. The gases evolved were absorbed in water. Twenty cc. of the solution thus obtained was treated with an excess of standard silver nitrate solution. The precipitated silver halides were filtered through a Gooch crucible, washed, dried and weighed. The excess silver nitrate in the filtrate was determined by titration with standard ammonium thiocyanate using ferric ammonium alum as an indicator. From these data the relative amounts of silver bromide and silver chloride in the precipitate were calculated. The results were as follows: ***Anal.*** AgX, 0.2837, 0.2909; cc. of 0.09976 N $AgNO_3$, 23.82, 23.88; cc. of 0.1197 *N* NH_4CNS, 3.32, 3.26; AgCl, calcd., 0.2835, 0.2855; AgBr, calcd., 0.0002, 0.00054. These results indicate that the hydrogen halide evolved is almost quantitatively hydrogen chloride and support the view that the bromination product is a dibromo derivative.

C. Preparation of **β-Bromo** Ethers. Condensation of **α,β-Dibromo-ethyl** Ether with an **Alkylmagnesium** Halide.—The Grignard reagents were prepared in the usual

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[18] Wislicenus, *Ann.*, 192, 111 (1878).

[19] This experiment is taken from the unpublished work of Dr. Harry B. Dykstra.

manner from the corresponding alkyl bromides. The α,β-dibromo ether was mixed with about twice its volume of anhydrous ether and placed in a two-liter flask surrounded by an ice-bath. The flask was provided with a reflux condenser and the Grignard reagent added dropwise, with constant shaking. The reaction took place instantaneously and with a hissing sound. The rate at which the reagent was added was regulated so as to avoid undue loss of ether by volatilization through the condenser. A slight excess of the alkylmagnesium halide not only served to increase the yield but also to render the product more easily purifiable. The reaction mixture was decomposed by pouring on ice and acidifying with dilute hydrochloric acid. The ether layer was separated, dried over calcium chloride and the ethyl ether removed by distillation. The product was then transferred to a smaller flask, about 5% of its weight of solid sodium hydroxide added and fractionated.

β-Ethoxy-*n*-propyl bromide and β-ethoxy-*n*-butyl bromide were distilled at atmospheric pressure, but the remaining compounds were distilled under diminished pressure. Further purification was effected by refractionation, sometimes over solid alkali, using an efficient column.

The bromine determinations were made by decomposing the compounds by the Bacon–Stephanow procedure and titrating the halogen by the Volhard method, using ferric nitrate as an indicator.

TABLE II

β-BROMO-ALKYL ETHYL ETHERS, $C_2H_5O—CHR—CH_2Br$

β-Ethoxy- ( )-bromide	R-	Yield, %	B. p., °C.	d^{20}_{20}	Bromine, %	
					Found	Calcd.
n-Propyl	CH_3-	77.4	138	1.2706	47.91	47.85
n-Butyl	C_2H_5-	60.5	166	1.2317	44.22	44.15
n-Amyl	*n*-C_3H_7-	66.5	176	1.1929	41.06	40.98
Iso-amyl	*iso*-C_3H_7-	30.0	172	1.2183	40.54	40.98
n-Hexyl	*n*-C_4H_9-	70.0	85–87 (15 mm.)	1.1573	38.22	38.24
Isoheptyl	*iso*-C_5H_{11}-	60.0	93–95 (15 mm)	1.1286	35.67	35.83

Ethyl-β-iodo-ethyl Ether,[20] $C_2H_5—O—CH_2—CH_2I$.—The methods described by Baumstark and by Henry for the preparation of this compound were tried but the following procedure was found to be much superior.

A mixture of 35 g. of anhydrous sodium iodide, 35 cc. of 95% alcohol and 24 g. of β-chloro-ethyl ethyl ether was refluxed on the water-bath for five hours. The reaction mixture was diluted with water, causing the separation of an oily layer. The aqueous layer was extracted with chloroform, the extract added to the oily layer and the solution thus obtained dried and fractionally distilled. Ten g. of the chloro ether was recovered. The yield was 24 g. or 89% of the theoretical based on the amount of chloro ether actually used. After further purification the ethyl β-iodo-ethyl ether boiled at 154.5–155° (corr.); d^{20}_{20} 1.7032. Demole gives the same boiling point. Henry gives the density as d^0 1.6924.

Preparation of β-Ethoxy-alkyl Mercaptans and their Derivatives

β-Ethoxy-alkyl Mercaptans, $C_2H_5—O—CHR—CH_2SH$.—A solution of potassium hydrosulfide was prepared by saturating a solution of potassium hydroxide in methyl alcohol with hydrogen sulfide. The appropriate β-chloro-ether was added to this solution in such amounts as would leave the hydrosulfide in approximatey 100% excess. The combined solutions were placed in pressure bottles in 100–150-cc. por-

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[20] Baumstark, *Ber.*, 7, 1172 (1874); Demole, ibid., 9, 746 (1876); Henry, Bull. *soc. chim.*, 44, 459 (1885); *Compt.* rend., 100, 1007 (1885).

tions and heated in a water-bath for the time indicated. The reaction mixture was diluted with water, causing a large part of the product to separate as an oily layer. The aqueous portion was extracted with petroleum ether and the extract added to the main product. Usually it was found advantageous to dissolve the mercaptan in caustic soda solution and reprecipitate with hydrochloric acid. When the reaction had been carried quite to completion this solution and reprecipitation proved unnecessary. The crude mercaptan was finally dried and fractionally distilled. A small amount of the sulfide was always formed as a by-product. The experimental conditions and yield values are shown in Table III.

TABLE III

β-ETHOXY-ALKYL MERCAPTANS, $C_2H_5—O—CHR—CH_2SH$

β-Ethoxy-( )-mercaptan	Formula	Chloro ether, g.	Temp., °C.	Time, hours	Yield, % mercaptan	Yield, % sulfide
Ethyl[7]	$C_2H_5OCH_2CH_2SH$	100	65	24	74	13
n-Propyl	$C_2H_5OCH(CH_3)CH_2SH$	25	..	50	36[a]	..
n-Butyl	$C_2H_5OCH(C_2H_5)CH_2SH$	50	90	60	61	14

[a] Eight grams of chloro ether recovered.

The β-ethoxy-alkyl mercaptans are colorless liquids, readily obtained in a high degree of purity. The boiling points are remarkably constant. These ethoxy mercaptans form insoluble salts of both mercury and lead but all attempts to obtain such salts in the crystalline condition failed.

Mercury β-Ethoxy-alkyl Mercaptide Chloride, $C_2H_5—O—CHR—CH_2SHgCl$.—The mercuric chloride derivatives were readily prepared by mixing an alcoholic solution of mercuric chloride with that of the mercaptan. The salt is deposited slowly as a crystalline white powder. These deposits were filtered off, washed first with alcohol and then .with ether, dried and submitted directly to analysis.

Bis-(β-ethoxy-alkyl) Disulfide, $(C_2H_5O—CHR—CH_2)_2S_2$.—The ethoxy mercaptans were oxidized quantitatively to the disulfides by shaking with the theoretical amount of iodine in either aqueous or alcoholic solution. The oily products which separated were washed with water, dried over calcium chloride and distilled under diminished pressure.

The physical constants and analyses of the β-ethoxy-alkyl mercaptans and their derivatives are summarized in Table IV.

TABLE IV

PHYSICAL CONSTANTS AND ANALYSES

β-Ethoxy-( ) mercaptan	Formula	B. p., °C. (uncorr.)	d_{20}^{20}	Sulfur, % Calcd.	Sulfur, % Found
Ethyl[7]	$EtOCH_2CH_2SH$	125.5–125.8	0.9479	30.20	30.24
n-Propyl	$EtOCHMeCH_2SH$	134.0–134 5	.9238	26.69	26.88
n-Butyl	$EtOCHEtCH_2SH$	156–157	.9177	23.89	25 95
Bis-(ethoxy-( )-) disulfide					
Ethyl	$(EtOCH_2CH_2)_2S_2$	161 (33 mm.)	1.0510	30 60	30.31
n-Butyl	$(EtOCHEtCH_2)_2S_2$	135 (8 mm.)	1 0013	...	..
Mercury ethoxy-( ) mercaptide chloride		M. p. (dec)			
Ethyl	$EtOCH_2CH_2SHgCl$	152.0–153 5	....	9.40	9 41
n-Propyl	$EtOCHMeCH_2SHgCl$	121–123	....	9.03	9.14
n-Butyl	$EtOCHEtCH_2SHgCl$	86-87	....	8 68	8.53

Bis-(β-Ethoxy-ethyl) Sulfide, $(C_2H_5O—CH_2—CH_2)_2S$.—A solution of 20 g. of sodium hydroxide in 100 cc. of 70% alcohol was saturated with hydrogen sulfide. To this solution 25 g. of α-ethoxy-ethyl chloride was added and the reaction mixture heated at the boiling point for three hours. As no effort was made to prevent the escape of hydrogen sulfide the active agent was sodium sulfide. After cooling the reaction mixture was diluted with water, causing the product to separate as an oily layer. The aqueous layer was extracted with ether and the extract added to the main product. The ether solution was dried and the product purified by fractional distillation. The yield was 51%; b. p. 229° (corr.); d_{20}^{20} 0.9840.

Anal. Subs., 0.1483: $BaSO_4$, 0.933. Calcd. for $C_8H_{18}O_2S$: S, 17.99. Found: S, 17.90.

Formation of Ethylene Sulfide.—Six g. of β-ethoxy-ethyl mercaptan was heated with 12 g. of 48% hydrobromic acid on a water-bath for three hours. A white solid separated, which was proved to be a mixture of the polymers of ethylene sulfide by complete conversion into diethylene disulfide by depolymerization with phenol.

Acetone **β-Ethoxy-ethyl** Mercaptol, $(CH_3)_2C(SCH_2—CH_2OC_2H_5)_2$.—A mixture of 11 g. of β-ethoxy-ethyl mercaptan and 5 g. of acetone was saturated with dry hydrogen chloride. The reaction mixture became warm and water separated. The mercaptol was washed with water, dried over calcium chloride and distilled *in vacuo*. The yield was 80%; b. p. 134° (7 mm.); d_{20}^{20} 1.0044.

Anal. Subs., 0.2173: $BaSO_4$, 0.4070. Calcd. for $C_{11}H_{24}O_2S_2$: S, 25.41. Found: S, 25.72.

Sodium **β-Ethoxy-ethyl Sulfonate,**[21] $C_2H_5—O—CH_2—CH_2SO_3Na$.—Fourteen grams of β-ethoxy-ethyl mercaptan was placed in a flask under a reflux condenser. While the contents of the flask was kept at the boiling point, a solution of 30 g. of concd. nitric acid in 100 cc. of water was added in small portions during the course of an hour. The digestion was continued at the boiling point until the reaction mixture became homogeneous. The solution was concentrated on the steam plate, neutralized with sodium hydroxide solution and evaporated to dryness. The sodium sulfonate was extracted with 90% alcohol. Evaporation of the alcoholic extract yielded 21 g. of crude product. Recrystallization from alcohol gave a pure product. The sodium was determined by ashing a weighed sample, treating with sulfuric acid and igniting.

Anal. Calcd. for $C_4H_9O_4SNa$: Na, 13.06. Found: Na, 13.64.

The sodium salt of β-ethoxy-ethyl sulfonic acid is very soluble in water, moderately soluble in 90% alcohol, but only slightly soluble in absolute alcohol. The free acid was not obtained in the pure condition.

β-Ethoxy-ethyl Sulfochloride, $C_2H_5—O—CH_2—CH_2SOCl$.—Twenty-one grams of dry, finely pulverized sodium β-ethoxy-ethyl sulfonate was mixed with 27 g. of phosphorus pentachloride in a round-bottomed flask. The reaction proceeded with the evolution of heat. The flask was arranged for vacuum distillation and heated gently at first but more strongly as the reaction neared completion. The portion distilling above 100° under strongly diminished pressure was washed with water, dried over calcium chloride and twice distilled *in vacuo*. A yield of 8 g. boiling at 118–122° (26 mm.) was obtained. The product was not pure since analysis showed a chlorine content of 21.64% while the calculated value is 20.54%.

A benzene solution of the β-ethoxy-ethyl sulfochloride described above was saturated with dry ammonia gas. The solution was filtered from the ammonium chloride and evaporated. The product obtained was an oil which crystallized after several

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[21] Hübner, *Ann.*, **223,** 218 (1884).

days standing as large colorless crystals, m. p. 41°. This substance, apparently the amide, was not obtained in sufficient purity for analysis.

Use of β-Halogen Ethers in the Malonic Ester Synthesis

β-Ethoxy-ethyl Malonic Ester,[22] $C_2H_5OCH_2—CH_2—CH(COOC_2H_5)_2$.—Seven and one-half grams of sodium was dissolved in 100 cc. of anhydrous alcohol and 50 g. of pure malonic ester added. The flask was shaken vigorously to break up the lumps of the sodium salt and 35 g. of β-chloro-ethyl ethyl ether added with warming and shaking until a clear solution was obtained. The reaction mixture was heated on the water-bath for three hours. The alcohol was distilled off, water added and the product extracted with petroleum ether. Two fractionations under diminished pressure yielded 11.4 g. (14%) of β-ethoxyethylmalonic ester boiling at 134–138° (15 mm.), d^{20}_{20} 1.0430. The boiling point given in the literature is 136° (13 mm.).

β-Ethoxy-*n*-butylmalonic Ester, $C_2H_5O—CHC_2H_5—CH_2—CH(COOC_2H_5)_2$.—A similar reaction was carried out using 50 cc. of anhydrous alcohol, 3 g. of sodium, 22 g. of malonic ester and 18.1 g. of α-bromo-β-ethoxy-*n*-butane. The product boiled at 146–150° (12 mm., uncorr.). Titration of the aqueous solution for ionized halogen showed only 64% of the bromo ether to have been destroyed. The reaction mixture was also quite alkaline, indicating that the heating should have been continued for a longer time. The yield was 58% on the basis of bromo ether actually destroyed. The product was not analyzed but was carried directly to the following preparation.

Calcium β-Ethoxy-*n*-butylmalonate, $C_2H_5O—CHC_2H_5—CH_2—CH(COO)_2Ca$.—The entire product from the preceding preparation was hydrolyzed by heating on the water-bath with a solution of sodium hydroxide (5 g. in 10 cc. of water) until the oily layer had disappeared. The solution was neutralized with concd. hydrochloric acid and the calcium salt precipitated by the addition of a concd. solution of calcium chloride. The salt was filtered off, washed and dried; yield, 6.5 g.

A portion of the salt recrystallized from a mixture of equal parts of methyl alcohol and water was obtained as a white crystalline powder. Calcium was determined by igniting a weighed sample, treating with sulfuric acid and re-igniting.

Anal. Calcd. for $C_9H_{14}O_5Ca$: Ca, 16.54. Found: Ca, 16.33.

γ-Ethoxy-*n*-caproic Acid, $C_2H_5—OCHC_2H_5—CH_2—CH_2—COOH$.—Eight cc. of concd. hydrochloric acid was added to the remainder of the calcium salt obtained in the previous preparation and the free substituted malonic acid extracted with ether. Upon evaporation of the ether, β-ethoxy-*n*-butylmalonic acid was obtained as a thick sirup which could not be induced to crystallize. The product was heated at 180" on an oil-bath as long as any gas was evolved (fifteen minutes); r-ethoxycaproic acid, b. p. 138–140° (8 mm.) uncorr., d^{20}_{20} 0.9816, was obtained in a yield of 3.3 g.

The barium salt was prepared by neutralizing a solution of barium hydroxide with *a* slight excess of the acid and carefully evaporating the solution. It is very soluble in water, alcohol and acetone. Barium was determined by ashing a weighed sample and igniting with sulfuric acid.

Anal. Calcd. for $C_{16}H_{30}O_6Ba \cdot H_2O$: Ba, 29.01. Found: Ba, 29.10.

The Williamson Reaction

β-Ethoxyphenetole, $C_6H_5—O—CH_2—CH_2—OC_2H_5$.—Ethyl β-chloro-ethyl ether was heated with an excess of an alcoholic solution of sodium phenolate for ten days. The greater part of the alcohol was removed by distillation and the residue diluted with water. The oily layer which separated was washed with dilute caustic soda solu-

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[22] German Patent 285,636; *Chem. Zentr.*, II, 639 (19151.

tion, dried and fractionally distilled. The product was obtained as a colorless liquid; b. p. 230–232° (corr.); d_{20}^{20} 1.0057.

Bentley, Haworth and Perkin,[23] who obtained the same product by an application of the malonic ester synthesis, give the b. p. as 230°. Henry,[9] who obtained the compound by the action of sodium ethylate upon β-chlorophenetole, gives the boiling point as 230°; d 1.018.

Reaction with Aniline

β-Ethoxy-ethylaniline, $C_6H_5NHC_2H_4—O—C_2H_5$.—Fifty grams of ethyl β-chloroethyl ether and an equal weight of aniline were heated at the boiling point for about ten hours. The temperature rose to 180°. The reaction mixture was decomposed by dilute sodium hydroxide solution and the mixture of bases separated, dried and submitted to fractional distillation. Repeated fractionation was necessary to separate the products. Mono-β-ethoxy-ethylaniline was obtained as a colorless liquid, b. p. 262–263° (corr.), d_{20}^{20} 1.0156. It darkens on standing and develops a disagreeable odor.

Anal. Subs., 0.3798: required 22.7 cc. of 0.10006 N H_2SO_4. Calcd. for $C_{10}H_{15}ON$: N, 8.49. Found: N, 8.36.

Mono-β-ethoxybutylaniline, $C_6H_5NH—CH(C_2H_5)—CH_2—OC_2H_5$.—This compound was prepared in an analogous manner but with much greater difficulties in purification, due to the formation of tarry substances. The compound boils at 264–269° (corr.) and has a density of d_{20}^{20} 0.9830.

Reaction with Magnesium

Preparation of **1,2-*Iso*heptene,** $(CH_3)_2CH—CH_2—CH_2—CH{=}CH_2$.—Thirty-five grams of β-ethoxy isoheptyl bromide was added in small portions to 12 g. of magnesium turnings covered with 75 cc. of dry ether. The magnesium soon became coated with a gummy white substance which rendered it somewhat inactive. After warming for five hours on the water-bath, the ether was distilled off using an efficient column. The remaining liquid was decanted from the residue and distilled until the temperature reached 120°. Further fractionation of the distillate yielded 5 g. of isoheptene boiling between 80 and 85°, mainly at 85°. The product was identified by conversion into the dibromide.

1,2-*Iso*heptene Dibromide, $(CH_3)_2CH—CH_2—CH_2—CHBr—CH_2Br$.—The *iso*heptene from the preceding preparation was dissolved in chloroform and treated with a slight excess of bromine. The crude dibromide was washed successively with concd. sulfuric acid, dilute sodium hydroxide and water and then dried. The product which distilled in *vacuo* with slight decomposition was obtained in a yield of 8 g., b. p. 95" (13 mm.), d_{20}^{20} 1.5083.

Anal. Calcd. for $C_7H_{14}Br_2$: Br, 61.96. Found: Br, 60.29.

Summary

The method of Houben and Fuhrer has been adapted to the synthesis of β-bromo-alkyl ethyl ethers and six new compounds of this type are described.

It is shown that, notwithstanding the relatively low chemical reactivity of the β-halogenated ethers in comparison with the a-halogenated derivatives, the β-bromo-alkyl ethers may be used advantageously in certain syntheses. They react readily with the alkali hydrosulfides to form β-ethoxy-alkyl mercaptans, which in turn may be converted into the corre-

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[23] Bentley, Haworth and Perkin, J. *Chem. Soc.*, 69, 171, 1503 (1896).

sponding disulfides, sulfonic acids and related derivatives. The β-bromo-alkyl ethers may be used in the same way as ordinary alkyl halides in the malonic ester synthesis, Williamson's reaction and in the formation of ethoxy-alkylanilines.

β-Bromo-alkyl ethyl ethers react in ether solution with magnesium to form olefins. Isoheptene is prepared in this way.

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[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY AT DUKE UNIVERSITY]

PICTET AND GAMS' BERBERINE SYNTHESIS

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The synthesis of the alkaloid berberine by Pictet and Gams[1a] has long been regarded as classic. Some doubt as to its accuracy has, however, recently arisen.

Buck and Perkin[2] in attempting to synthesize *epi*-berberine (2,3-dimethoxy-9,10-methylenedioxyprotoberberine)[3] by the method of Pictet and Gams[1] obtained only the isomeric pseudo-*epi*-berberine (2,3-dimethoxy-10,11-methylenedioxyprotoberberine). Haworth, Perkin and Rankin[4] in repeating Pictet and Gams' synthesis of berberine (2,3-methylenedioxy-9,10-dimethoxyprotoberberine) obtained exclusively the isomeric pseudoberberine (2,3-methylenedioxy-10,11-dimethoxyprotoberberine), the second ring closure taking place so as to give the 10,11- and not the 9,10-dimethoxy compound. A search of the literature showed that Pictet and Gams' alleged ring closure to give the 9,10 compound is unique, at least when the ring substituents are methoxyl or methylenedioxy groups. Pictet himself expresses astonishment that berberine and not the isomer should be formed. The only departure from the general rule is the formation of both tetrahydropalmatine and nor-coralydine from tetrahydropapaveroline, recorded by Spath and Kruta.[5] Here, however, hydroxyl, not alkoxyl, groups were the substituents.

It therefore appeared necessary to investigate the synthesis further, in order to detect any error, if such were present. The authors believe that they have definitely shown the synthesis to be erroneous.

Pictet and Gams[1] on heating homoveratroylhomopiperonylamine with

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[1] The material presented in this paper is from a dissertation submitted by Rose M. Davis to the Graduate School of Arts and Sciences of Duke University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1929.

[1a] Pictet and Gams, Ber., **44**, 2480 (1911).

[2] Buck and Perkin, *J. Chem. Soc.*, **125**, 1675 (1924).

[3] The nomenclature of Buck, Perkin and Stevens, *ibid.*, **127**, 1462 (1925), is used in the present paper.

[4] Haworth, Perkin and Rankin, *ibid.*, **125**, 1686 (1924).

[5] Späth and Kruta, Monatsh., 50, 341 (1928).

phosphorus pentoxide, obtained an amorphous glassy mass, melting at 68–70', which they considered to be 6,7-methylenedioxy-3′,4′-dimethoxy-3,4-dihydroprotopapaverine. Haworth, Perkin and Rankin,[4] carrying out the same cyclization, obtained a white crystalline compound, melting at 88°, and this was shown[6] to be rapidly oxidized in air to give 6,7-methylenedioxy-3′,4′-dimethoxy-9-keto-3,4-dihydroprotopapaverine. It may, therefore, be safely inferred that Pictet and Gams' product contained considerable amounts of this oxidized base, especially as it had been exposed in a desiccator. 6,7-Methylenedioxy-3′,4′-dimethoxy-3,4-dihydroprotopapaverine, as has clearly been shown by Haworth and co-workers,[4,6] gave only 6,7-methylenedioxy-3′,4′-dimethoxy-1,2,3,4-tetrahydroprotopapaverine on reduction, and this, on treatment with methylal or formaldehyde, results exclusively in 2,3-methylenedioxy-10,11-dimethoxytetrahydroprotoberberine (pseudoberberine). The obvious inference is that Pictet and Gams mistook tetrahydropseudoherberine for tetrahydroberberine. The authors constantly obtained tetrahydropseudoberberine on repeating Pictet and Gams' work. The other source of error is the presence of the oxidized cyclized material, which had been overlooked by Pictet and Gams. This has been shown by Ruck and co-workers[6] (and carefully checked by the present authors) to give rise to 6,7-methylenedioxy-3′,4′-dimethoxy-9-ketoprotopapaverine under the action of alkalies, with surprising ease. As far as is possible to see from Pictet and Gams' meager account, this compound is identical with their "veratryl-nor-hydrohydrastinine," the supposed reduction product of 6,7-methylenedioxy-3′,4′-dimethoxy-3,4-dihydroprotopapaverine. The compound is incapable of reacting with methylal, the requisite imino group being absent. Pictet and Gams' analysis is correct for veratryl-nor-hydrohydrastinine.

It is true that Pictet and Gams reduced their crude cyclization product before treating it with alkali, but the authors have observed that 6,7-methylenedioxy-3′,4′-dimethoxy-9-keto-3,4-dihydroprotopapaverine is not reduced under the conditions employed. It would seem highly probable, therefore, that Pictet and Gams obtained not veratryl-nor-hydrohydrastinine (6,7-methylenedioxy-3′,4′-dimethoxy-1,2,3,4-tetrahydroprotopapaverine) but 6,7-methylenedioxy-3′,4′-dimethoxy-9-keto-protopapaverine on cyclization, reduction and treatment with alkali. As before stated, this cannot react with methylal. It is concluded, therefore, that Pictet and Gams never isolated veratryl-nor-hydrohydrastinine, but obtained the oxidized side product, a compound closely related to xanthaline. Their tetrahydroberberine must, therefore, have been actually tetrahydropseudoberberine and have been obtained by operating with crude reaction mixtures.

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[6] Buck, Haworth and Perkin, *J. Chem. Soc.*, **125**, 2176 (1924)

There remained one possibility, that Pictet and Gams had by chance obtained some unknown reduction product capable of giving tetrahydroberberine on treatment with methylal. The authors therefore carefully investigated the reduction products of 6,7-methylenedioxy-3′,4′-dimethoxy-9-keto-3,4-dihydroprotopapaverine and of 6,7-methylenedioxy-3′,4′-dimethoxy-9-keto-protopapaverine. From the first, 6,7-methylenedioxy-3′,4′-dimethoxy-9-hydroxy-1,2,3,4-tetrahydroprotopapaverine was obtained and from the second, 6,7-methylenedioxy-3′,4′-dimethoxy-9-hydroxyprotopapaverine. This, analogous to the compound papaverinol described by Stuchlik,[7] cannot react with methylal. 6,7-Methylenedioxy-3′,4′-dimethoxy-9-hydroxy-1,2,3,4-tetrahydroprotopapaverine indeed reacts with methylal or formaldehyde, giving rise to an interesting compound described in the experimental part, but this compound is very different from the tetrahydroberberine.

Experimental

Veratryl-nor-hydrohydrastinine (6,7-Methylenedioxy-3′,4′-dimethoxy-1,2,3,4-tetrahydroprotopapaverine).—The details given by Pictet and Gams regarding this compound are meager. A number of experiments, following as closely as possible the procedure given, were carried out with the uniform result that the material obtained on cyclizing homoveratroylhomopiperonylamine with phosphorus pentoxide and then reducing with tin and hydrochloric acid, detinning with hydrogen sulfide and liberating the bases by alkali, was found to be a mixture of 6,7-methylenedioxy-3′,4′-dimethoxy-1,2,3,4-tetrahydroprotopapaverine (melting at 84° and described by Haworth and co-workers[4,6]) and 6,7-methylenedioxy-3′,4′-dimethoxy-9-keto-protopapaverine, melting at 208°. The former has been dealt with in another place; the latter cannot react with methylal (this was checked experimentally).

Authentic 6,7-methylenedioxy-3′,4′-dimethoxy-3,4-dihydroprotopapaverine when reduced with tin and hydrochloric acid gave 6,7-methylenedioxy-3′,4′-dimethoxy-1,2,3,4-tetrahydro-isoquinoline, melting at 84° (see above), together with varying amounts of 6,7-methylenedioxy-3′,4′-dimethoxy-9-keto-3,4-dihydroprotopapaverine, melting at 151° and formed by air oxidation of unchanged material. If alkali had been used (sodium hydroxide) in liberating the base, then in place of the latter compound (and formed from it) 6,7-methylenedioxy-3′,4′-dimethoxy-9-keto-protopapaverine melting at 208° was found. Neither this nor the dihydro compound is capable of reacting with methylal.

Pictet and Gams' Preparation of Tetrahydroberberine.—The preparation of tetrahydroberberine described by Pictet and Gams was very carefully repeated a number of times, following the rather vague directions as closely as possible except that the reduction was carried out immediately on the cyclized product and no attempt was made to isolate the supposed veratryl-nor-hydrohydrastinine, m. p. 208" (see above). After cyclizing homoveratroylhomopiperonylamine, reducing, detinning and treatment of the base with methylal, the pseudotetrahydroberberine (2,3-methylenedioxy-10,11-dimethoxytetrahydroprotoberberine) of Haworth and co-workers, melting at 168°, was always obtained. Mixed with authentic tetrahydroberberine, m. p. 167°, the mixture showed a considerable depression (10°). If the original cyclization product had been kept in a desiccator, as described by Pictet and Gams, or any other oppor-

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[7] Stuchlik, *Monatsh*, **21**, 814 (1900).

tunity for air oxidation given, then 6,7-methylenedioxy-3',4'-dimethoxy-9-keto-protopapaverine, m. p. 208°, was also found.

In connection with compounds of the foregoing types, the authors have frequently found that mixed melting point determinations of their salts, especially the picrates, are quite unreliable. This point seems to have escaped some workers.

6,7-Methylenedioxy-3',4'-dimethoxy-9-hydroxy-1,2,3,4-tetrahydroprotopapaverine.—6,7-Methylenedioxy-3',4'-dimethoxy-9-keto-3,4-dihydroprotopapaverine was reduced in 10% sulfuric acid solution with powdered zinc, a little copper sulfate being added to the mixture. When the reaction slackened, the whole was heated on a water-bath for one hour. After cooling, the mixture was filtered and treated with sodium hydroxide solution to liberate the bases. A gummy crystalline mass separated and was carefully fractionated from alcohol. Three compounds were found: (1) unchanged material, (2) 6,7-methylenedioxy-3',4'-dimethoxy-9-keto-protopapaverine, melting at 208°, and formed from the unchanged material by the action of the alkali and (3) a base $C_{19}H_{21}O_5N$. The latter, 6,7-methylenedioxy-3',4'-dimethoxy-9-hydroxy-1,2,3,4-tetrahydroprotopapaverine forms white glittering broken prisms melting at 161–162° to a yellow liquid. It is moderately soluble in alcohol and benzene, readily soluble in chloroform and slightly soluble in ether. Acetic anhydride and hydrochloric acid give colorless solutions.

Anal. Calcd. for $C_{19}H_{21}O_5N$: C, 66.4; H, 6.1. Found: C, 66.3; H, 6.2.

It was not found possible to obtain the above compound by reduction with tin and hydrochloric acid, unchanged material being always recovered, although there was some destruction. The failure is doubtless due to the separation of the highly insoluble tin double salt.

The catalytic method of reduction of Adams and co-workers (hydrogen–platinum oxide) was found to give excellent results with acetic acid as solvent, four atoms of hydrogen being smoothly absorbed. No compound other than that described above was isolated.

2,3-Methylenedioxy-10,11-dimethoxy-13-hydroxytetrahydroprotoberberine.—6,7-Methylenedioxy-3',4'-dimethoxy-9-hydroxy-1,2,3,4-tetrahydroprotopapaverine, dissolved in methyl alcohol, was mixed with sodium bicarbonate and 40% formaldehyde solution gradually added. The mixture was heated on the water-bath and then precipitated with water and salt. The product was heated with concentrated hydrochloric acid for a few minutes. Upon cooling yellow crystals formed and these were recrystallized from hot dilute hydrochloric acid. These were decomposed with potassium carbonate solution and the product recrystallized from methyl alcohol. A mass of fine yellow needles separated, melting at 153°. When methylal was substituted for formaldehyde, the product was obtained with considerable difficulty and in very poor yield. It is readily soluble in chloroform, moderately soluble in alcohol and benzene and sparingly soluble in ether.

Anal. Calcd. for $C_{20}H_{21}O_5N$: C, 67.6; H, 5.9. Found: C, 67.5; H, 6.0.

The test suggested by Robinson[8] to distinguish between 1,2,3,4- and 1,2,4,5-ring closures was applied to the above compound and indicated it to be a 1,2,4,5-derivative.

6,7-Methylenedioxy-3',4'-dimethoxy-9-hydroxyprotopapaverine.—6,7-Methylenedioxy-3',4'-dimethoxy-9-keto-protopapaverine was reduced in hot acetic acid solution by the catalytic method of Adams. Two atoms of hydrogen (maximum) were absorbed. After diluting and filtering, excess of ammonia was added and the gummy product which separated was recrystallized several times from alcohol. The

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[8] Kaworth and Perkin, *J. Chem. Soc.*, **127**, 1448 (1925).

compound forms fine white needles from alcohol, melting at 161°. It is very soluble in chloroform, moderately soluble in benzene and fairly soluble in ether.

Anal. Calcd. for $C_{19}H_{17}O_5N$: C, 67.3; H, 5.0. Found: C, 67.3; H, 5.1.

Summary

The synthesis of berberine described by Pictet and Gams is in all probability erroneous, the error arising from overlooking the 6,7-methylenedioxy-3′,4′-dimethoxy-9-keto-3,4-dihydroprotopapaverine formed by air oxidation of their cyclized product. The "veratryl-nor-hydrohydrastinine" described by them is 6,7-methylenedioxy-3′,4′-dimethoxy-9-keto-protopapaverine, which cannot react with methylal. Any product which was obtained by the action of methylal must have been pseudoberberine and have been obtained by operating with crude reaction mixtures.

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[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

STUDIES IN THE DIPHENYL SERIES. SOME ARSENIC DERIVATIVES OF DIPHENYL

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Diphenyl, a substance now available in quantity at a low cost, is the starting point for the preparation of arsenic-containing compounds of possible therapeutic value Yet despite the vast amount of attention received by arsenicals during the past two decades, apparently only one paper has appeared in the literature on diphenyl derivatives of arsenic. Adams and Bauer[1] developed a method of entering this series, using the method of Bart with benzidine. Consequently a study has been made of tri-biphenylarsine and related compounds.

The actual starting material used in this investigation was *p*-bromoaniline, which was converted into 4-bromodiphenyl through the diazo reaction.[2] A pure product was obtained, but the process is time consuming, especially if the bromo-aniline has to be prepared, and the final yield is not particularly inspiring. Since then 4-chlorodiphenyl has appeared in the market and at a price much lower than bromo-aniline. While only one experiment was conducted, chlorodiphenyl appeared to be just as effective as the bromo derivative for a synthetic reagent. Several general methods have long been known for the preparation of arylated arsenic from aryl halides. One of these was ruled out because of inability to obtain biphenylmercuric acetate, while poor results attended the use

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[1] Adams and Bauer, THIS JOURNAL, 46, 1925 (1924).

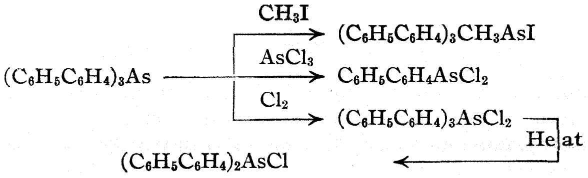
[2] Gomberg, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 42.

of magnesium. Excellent results, however, were obtained with sodium, over 80% in some instances.

$$AsCl_3 + 3C_6H_5C_6H_4Br + 6Na = As(C_6H_4C_6H_5)_3 + 3NaCl + 3NaBr$$

It was found that benzene could be substituted for ether in the synthesis. An unexpected result was the discovery of diphenyl in working up the mother liquors from the purification of tri-biphenylarsine. It does not seem likely that diphenyl formation could have resulted from the action of moisture on tri-biphenylarsine, for the latter was found to be insensitive to water at 80° in the presence of alkali. Neither does it appear at all probable that nascent hydrogen resulting from the interaction of water and sodium could replace bromine with hydrogen. It is possible to interpret the appearance of diphenyl as evidence of the formation of free biphenyl which subsequently picked up hydrogen.

The following diagram indicates how the various classes of organic derivatives were prepared from tri-biphenylarsine.



The chlorine and bromine addition products are not sensitive to moisture when free from solvent, but when hydrolysis does take place both halogen atoms are involved. Thus if tri-biphenylarsine dibromide is mixed with a small volume of alcohol, it quickly dissolves and in a few minutes a crystalline precipitate forms. It contains bromine but the amount is approximately one-half of the theoretical, assuming that tri-biphenylarsine hydroxy bromide was formed. The halogen content varies in different preparations, but some bromine persists after recrystallization. The product may be regarded as a mixture of the hydroxide and hydroxy bromide, although the latter was not isolated.

Experimental

Tri-biphenyl.—To 4.2 g. of granulated sodium suspended in **150** cc. of *dry* benzene were added 21 g. of 4-bromo-diphenyl and 5.5 g. of arsenic chloride. As the initial reaction was somewhat sluggish, it was speeded up by heating the mixture under a reflux condenser. The source of heat was removed as soon as boiling started. A vigorous reaction ensued and continued spontaneously for over half an hour. Heat was again applied for some time, after which the mixture while still warm was filtered by suction. The residue was washed with 100 cc. of hot benzene, the combined filtrate concentrated to approximately 35 cc. and **25** cc. of ordinary alcohol added. The resulting bulky crystalline precipitate was filtered, washed thoroughly with cold ethyl alcohol and dried; yield, **12** g. of fairly pure material.

Anal. Calcd. for $C_{36}H_{27}As$: As, 14.0. Found: As, 13.8.

This last filtrate was evaporated to dryness and the residue steam distilled. About one-half a gram of residual tri-biphenylarsine was found. The distillate contained **2.6** g.

of a substance identified by its odor and properties as diphenyl. It evidently contained traces of 4-bromodiphenyl as it responded to the Beilstein test for halogen and the melting point was low (68–69°) even after recrystallization from alcohol. However, the melting point was not changed after mixing with diphenyl, while on nitration a substance was obtained identical in all respects with a known sample of 4-nitrodiphenyl.

Tri-biphenylarsine was also obtained in good yield by substituting 4-chlorodiphenyl for the bromo compound in the above preparation. Less desirable results attended the use of the reagent of Grignard. Thus in one experiment to 10 g. of 4-iododiphenyl in ether solution was added 1 g. of magnesium turnings. Precautions were taken to have the reagents dry and the apparatus was swept out with dry air. Activated magnesium was added, but the resulting action was slow and incomplete. Barely enough heat was evolved to warm the mixture, to which arsenic chloride was added after standing overnight. This caused some heat evolution, and the formation of a bulky precipitate. Previous to decomposition with water the mixture was heated under a reflux condenser for an hour, then it was steam distilled. Diphenyl, 1.2 g. in amount, came over first followed by approximately 5 g. of iododiphenyl. The two substances were easily distinguished as the latter, melting as it does above the boiling point of water at atmospheric pressure, formed a sublimate. The difference in vapor pressure of the two substances at this temperature made a separation practicable. The residue (2 g.) was found to contain tri-biphenylarsine. Similar results were obtained with bromodiphenyl.

Tri-biphenylarsine dissolves readily in hot glacial acetic acid, methyl iodide, benzene and chloroform. It is less soluble in ether and practically insoluble in cold ethyl alcohol. It dissolves in about two volumes of hot benzene, separating in aggregates of tiny needle-like crystals melting at 182–183° with preliminary softening. At the boiling point decomposition takes place with the formation of free arsenic.

Action of Water.—The interpretation of some of the results obtained necessitated a knowledge of whether or not hydrolysis of tri-biphenylarsine took place. It was found that hydrolysis did not take place on heating the substance for many hours under a reflux condenser with alcoholic potash. At higher temperatures and pressure, on the contrary, positive results were obtained with dilute hydrochloric acid. A gram of tri-biphenylarsine was heated in a sealed tube with water containing hydrochloric acid to 250" for twelve hours. On opening the tube and steam distilling the contents a sufficient amount of volatile material was collected to be identified by the odor and a mixed melting point as diphenyl.

Tri-biphenylarsine-dibromide.—To 5 g. of tri-biphenylarsine dissolved in 40 cc. of pure dry chloroform was added 1.5 g. of dry bromine. Instant absorption took place with considerable heat evolution. The resulting cream-colored precipitate of flattened needles was filtered and dried; yield, 5.5 g.

Anal.[3] **Calcd** for $C_{36}H_{27}AsBr_2 \cdot CHCl_3$: Br, 19.7. Found: Br, 19.8.

The dibromide has no definite melting point, gradually softening above 200°. It was not obtained free from chloroform of crystallization. An excess of bromine inhibits completely crystal formation in the preparation of the dibromide, while the presence of moisture brings about tar formation. Once formed and freed from the solvent the solid substance is surprisingly insensitive toward moisture, perhaps because it is so insoluble in water. At any rate, it is unaffected by cold water or long standing exposed to the atmosphere. It is decomposed by hot water and by ordinary alcohol at room temperature.

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[3] A weighed amount of the substance after short. heating with alcoholic ammonia was evaporated to dryness, extracted with water containing a few drops of nitric acid and the filtered solution used in the regular way.

Tri-biphenylarsine-dichloride.—On bubbling chlorine through a chloroform solution of 5 g. of tri-biphenylarsine until no further absorption took place, a white crystalline precipitate quickly formed; yield, 6 g.

Anal. (for labile chlorine). Calcd. for $C_{36}H_{27}AsCl_2{\cdot}CHCl_3$: Cl, 9.8. Pound: Cl, 9.8.

The chlorine addition product melts at 272–273° with preliminary softening. It is only sparingly soluble in cold chloroform; accordingly an excellent yield is obtainable.

Action of Water.—The dichloride or dibromide was changed to a gum, which subsequently became crystalline on boiling with water. Chloroform was set free as well as halogen acid. Similar changes took place in cold alcohol, except that the new substance separated out directly in the solid phase. It was identified as tri-biphenylarsine dihydroxide, although an impure form as halogen was present even after recrystallization from alcohol. No evidence was found of the existence of the hydroxy bromide of tri-biphenylarsine.

Tri-biphenylarsine Dihydroxide.—Several grams of dichloride was heated on a steam-bath for a few minutes with a small volume of alcohol containing a few drops of ammonium hydroxide solution. The substance promptly dissolved, but a crystalline precipitate quickly appeared. It was purified by dissolving in the minimum amount of hot alcohol and adding water drop by drop until a slight turbidity resulted.

Anal. Calcd. for $C_{36}H_{29}O_2As$: As, 13.2. Found: As, 13.1.

It is sparingly soluble in alcohol, separating in microscopic prismatic needles melting at 262–263° with preliminary softening. It is easily dissolved by chloroform. Tri-biphenylarsine dihydroxide is also formed by the action of potassium permanganate on tri-biphenylarsine.

Tri-biphenylarsine Sulfide.—This was prepared by running hydrogen sulfide into an alcohol solution of the dihydroxide. The resulting precipitate of small rod-shaped crystals was filtered, washed and dried.

Anal. Calcd. for $C_{36}H_{27}AsS$: S, 5.7. Found: S, 5.5.

The sulfide is insoluble in most of the common solvents with the exception of chloroform, from which it is precipitated by alcohol as a crystalline powder melting at 239–240". Both the sulfide and dihydroxide are reduced by tin and hydrochloric acid in glacial acetic acid to tri-biphenylarsine.

Tri-biphenylmethylarsonium Iodide.—Obtained by heating for several hours under a reflux condenser 1 g. of tri-biphenylarsine dissolved in benzene with an excess (3 molar equivalents) of methyl iodide. Crystal formation started in a few minutes if the mixture was seeded, otherwise an oil separated out at first; yield, 0.8 g.

Anal. Calcd. for $C_{37}H_{30}AsI$: I, 18.8. Found: I, 18.9.

The arsonium compound is sparingly soluble in hot alcohol, separating in glittering gold-yellow plates melting at 151–152° with foaming. It decomposes at the melting point into methyl iodide and tri-biphenylarsine.

Tri-biphenylmethylarsonium iodochloride was obtained by bubbling chlorine through a warm solution of the arsonium iodide.

Anal. Calcd. for 0.1 g. of $C_{37}H_{30}AsICl_2$: AgI + AgCl, 0.0696 g. Found: AgI + AgCl, 0.0708.

It crystallizes from alcohol as a yellow powder melting at 86–88".

Tri-biphenylarsonium Hydroxide.—Two grams of the arsonium iodide derivative was shaken in alcohol with moist silver oxide, The mixture was filtered after the disappearance of the yellow color and evaporated in *vacuo* over sulfuric acid to a brittle colorless glass-like solid. This material probably contained some carbonate and sulfate picked up during the manipulation.

Anal. Calcd. for $C_{37}H_{31}OAs$: As, 13.3. Pound: As, 12.8.

No definite melting point was observed. It gradually softens on heating and foams at 120°, at which point it decomposes into methyl alcohol and tri-biphenylarsine. It is alkaline, absorbing carbon dioxide from the air on standing and turning red litmus paper blue.

Di-biphenylarsenious Chloride.—Ten grams of tri-biphenylarsine dichloride was heated to melting in a beaker; then the temperature was carefully raised until gentle boiling took place. Chloroform and chlorodiphenyl vapors were evolved. After several minutes of heating at this temperature the mixture was cooled and the resulting tar repeatedly extracted with absolute alcohol. A yellowish gummy material was deposited as the alcoholic extract cooled. The resulting solution was colorless and on concentration a white precipitate of small needle-like crystals usually was obtained. Altogether less than a gram of substance was obtained. Approximately a gram of diphenyl was isolated by the steam distillation of the residues.

Anal. Calcd. for $C_{24}H_{18}AsCl$: Cl, 8.5. Found: Cl, 7.8.

The chloride obviously was not obtained in a pure form. The substance as isolated softened above 110°, melting at 123°. It decomposes at the boiling point *in vacuo* and is easily dissolved by benzene or chloroform. It is sparingly soluble in alcohol. It is rapidly attacked by hot water, more slowly by ordinary alcohol, changing into the oxide and liberating hydrochloric acid. The hot vapors of the substance are irritating to the throat, but have no apparent effect on the skin.

Di-biphenylarsenious Oxide.—Prepared by heating the chloride with alcoholic ammonia, recrystallizing from alcohol.

Anal. Calcd. for $C_{48}H_{36}As_2O$: As, 19.3. Found: As, 19.4.

It is soluble in hot alcohol, separating as an oil in which crystalline aggregates form on standing. It gradually softens above 90° without any definite melting point.

Di-biphenylarsenious Sulfide.—Obtained as an amorphous powder by the action of hydrogen sulfide on an alcohol solution of the oxide. No definite melting point was observed, the substance gradually softening above 110".

Anal. Calcd. for $C_{48}H_{36}As_2S$: S, 4.0. Found: S, 4.5.

Di-biphenylarsinic acid was produced by passing moist chlorine through the chloride dissolved in chloroform. The oil resulting from evaporation of the solvent was dissolved in dilute sodium hydroxide solution, filtered and precipitated as an amorphous powder by dilute sulfuric acid. It was heated to melting and on cooling became crystalline.

Anal. Calcd. for $C_{24}H_{19}O_2As$: As, 9.1. Found: As, 9.1.

It softens above 95°, partially melting at 110°. This acid is soluble in alcohol and in water containing alkali-forming water-soluble salts.

Mono-biphenylarsenious Oxide.—A solution of 10 g. of tri-biphenylarsine in 50 g. of arsenic chloride was heated in a sealed tube to 300° for thirty-six hours. The mixture was then distilled up to 300° to remove arsenic chloride. Some diphenyl was also removed by this treatment. The residue (12 g.) was first washed with water containing hydrochloric acid to remove arsenious oxide; then it was extracted with alcohol. By this process any unchanged tri-biphenylarsine was left behind. The alcohol extract was concentrated and steam distilled to remove traces of diphenyl. A cream colored residue of 6 g. was obtained. It was finally purified by concentration of an alcohol solution.

Anal. Calcd. for $C_{12}H_9AsO$: As, 30.7. Found: As, 30.4.

It separates from alcohol, in which it is readily soluble, as an amorphous white powder melting at 163–165° with preliminary softening.

Mono-biphenylarsenious sulfide was prepared by the action of hydrogen sulfide on a dilute alcohol solution of the oxide. Ball-like aggregates of microscopic needles separated out. No definite melting point was observed, the substance softening above 108°.

Anal. Calcd. for $C_{12}H_9AsS$: S, 12.3. Found: S, 12.0.

Mono-biphenylarsenic Acid.—To a gram of the arsenious oxide derivative suspended in water containing a little ethyl alcohol was conducted a slow stream of chlorine for an hour. Then an excess of dilute sodium hydroxide solution was added and the mixture saturated with carbon dioxide. It was filtered and hydrochloric acid added. The resulting bulky precipitate was filtered with difficulty by suction and precipitated from alcohol by water.

Anal. Calcd. for $C_{12}H_{11}O_3As$: As, 27.0. Found: As, 27.2.

The new acid separates from alcohol as an amorphous powder partially melting at 180–181° with preliminary softening.

It is planned to continue work with these substances, also to investigate the diphenyl derivatives of antimony and bismuth.

Summary

It has been found that tri-biphenylarsine is obtainable in good yield from the interaction of arsenic chloride, 4-bromodiphenyl and sodium. Using tri-biphenylarsine as a starting point, some representative tri- and pentavalent arsenic derivatives have been prepared containing one, two and three biphenyl groups.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

CATALYTIC REDUCTION OF O-ALKYL SUBSTITUTED OXIMES[1]

BY LAUDER W. JONES AND RANDOLPH T. MAJOR

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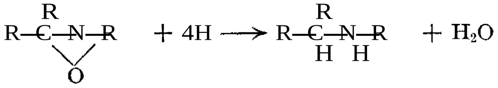
The reduction of N-alkyl substituted oximes was studied about thirty years ago by Dunstan and Goulding,[2] who found that sodium amalgam in absolute alcohol converted them into dialkylamines, according to the eauation



$$R{-}\underset{\diagdown\;\diagup \atop O}{\overset{R}{C}{-}N}{-}R + 4H \longrightarrow R{-}\underset{H}{\overset{R}{C}}{-}\underset{H}{N}{-}R + H_2O$$

The corresponding reduction of the O-alkyl substituted oximes apparently has not been investigated.

It has long been known, however, that oximes could be reduced to primary amines by the use of a number of different reducing agents.[3] Re-

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[1] presented at the Columbus meeting of the American Chemical Society, May, 1929.

[2] Dunstan and Goulding, *J. Chem. Soc.*, **79**, 639, **640** (1901).

[3] Meyer and Jacobson, "Lehrbuch der Organischen Chemie," Verlag von Veit and Company, Leipzig, **1907**, Vol. I, Part 1, p. 349.

cently Vavon and his co-workers[4] have shown that hydrogen in the presence of a platinum catalyst reduced the hydrochlorides of oximes in dilute alcohol to N-substituted hydroxylamine hydrochlorides.

It was thought, therefore, that by using somewhat similar methods it might be possible to reduce O-alkyl oxime hydrochlorides to O,N-dialkylhydroxylamine hydrochlorides according to the equation

$$\text{R—CR=NOR·HCl} + \text{H}_2 \xrightarrow{\text{Pt}} \text{RHCR—NHOR·HCl}$$

Solutions of the O-alkyl oxime hydrochlorides were prepared in two ways. The first was to dissolve the O-alkyl oxime in a solution of the calculated amount of hydrogen chloride in 65% alcohol. The other method was to add the calculated amount of the carbonyl derivative to a solution of O-alkylhydroxyl-ammonium chloride in 65% alcohol, and to allow the solution to stand long enough to come to equilibrium, usually about an hour. However, it was found that it did not make any difference in the reductions which way the O-alkyl oxime hydrochloride was prepared.

The reductions were carried out by agitating the solution containing the platinum catalyst at room temperature in an Adams Reduction Apparatus.[5] When the solution had absorbed the calculated amount of hydrogen the platinum was removed by filtration and the alcohol and most of the water evaporated. By means of alkali the free bases were obtained from the hydrochlorides, which remained as residues. In this way O-methyl-N-amyl-3-hydroxylamine, $(C_2H_5)_2CH·NHOCH_3$, O-methyl-N-isopropylhydroxylamine, $(CH_3)_2CH·NHOCH_3$, O-methyl-N-heptyl-4-hydroxylamine, $(C_3H_7)_2CH·NHOCH_3$, and O-ethyl-N-*iso*propyl-hydroxylamine, $(CH_3)_2CH·NHOC_2H_5$ were prepared.

To serve as a means of identification, several derivatives of these compounds were made. The chloroplatinates of all of these substituted hydroxylamines except O-methyl-N-heptyl-4-hydroxylamine, which did not yield a solid chloroplatinate, were prepared. In addition, the phenyl isocyanate addition products, which have the general formula $RRCH·NOR·CO·NHC_6H_5$, of all of them except O-ethyl-N-*iso*propylhydroxylamine were formed. Also, the phenyl mustard oil addition product of O-methyl-N-amyl-3-hydroxylamine, which has the formula $(C_2H_5)_2CH·NOCH_3·CS·NHC_6H_5$, was made.

It was found that the properties of the O-ethyl-N-*iso*propylhydroxylamine that was made in this manner were identical with those ascribed to this compound by Hecker, who made it in another way.[6] O-Methyl-N-amyl-3-hydroxylamine and O-methyl-N-*iso*propylhydroxylamine, which

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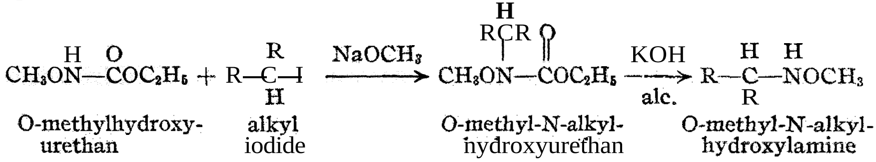
[4] Vavon and Krajcinovic, *Bull. soc. chim.*, [4] 43, 231 (1928); this paper also contains references to earlier articles on this subject by Vavon and his co-workers.

[5] Manufactured by the Standard Calorimeter Company, East Moline, Ill.

[6] Hecker, *Am. Chem. J.*, 50, 455 (1913).

previously had not been described, were also prepared, according to the equations



$$\overset{\text{H}}{\text{CH}_3\text{ON}}\!-\!\overset{\text{O}}{\text{COC}_2\text{H}_5} + \text{R}\!-\!\underset{\text{H}}{\overset{\text{R}}{\text{C}}}\!-\!\text{I} \xrightarrow{\text{NaOCH}_3} \text{CH}_3\overset{\overset{\text{H}}{\text{RCR}}}{\text{ON}}\!-\!\overset{\text{O}}{\text{COC}_2\text{H}_5} \xrightarrow[\text{alc.}]{\text{KOH}} \text{R}\!-\!\underset{\text{R}}{\overset{\text{H}}{\text{C}}}\!-\!\overset{\text{H}}{\text{N}}\text{OCH}_3$$

O-methylhydroxyurethan — alkyl iodide — O-methyl-N-alkylhydroxyurethan — O-methyl-N-alkylhydroxylamine

The properties of the hydroxylamines synthesized in this manner were the same as those of the corresponding compounds synthesized by reducing the O-alkyl oximes.

Another reaction always accompanied the formation of the O,N-dialkylhydroxylammonium chlorides when O-alkyl oxime hydrochlorides were reduced. Ammonium chloride, a ketone and an alcohol were always formed. This side reaction was most pronounced in the case of the reduction of methyl and ethyl acetoxime hydrochlorides, when about 75% of the oximes were transformed into these products. Also, O-methylacetaldoxime hydrochloride, when reduced in the same way, gave almost a quantitative yield of ammonium chloride. Presumably the formation of these products depends upon the fact that in the solution there is an equilibrium of the type shown in the equation

$$\text{R—CR=NOR·HCl} + \text{H}_2\text{O} \rightleftarrows \text{R—CR=O} + \text{RONH}_2\text{·HCl}$$

That this is probable is suggested by the fact that the usual method used to hydrolyze the O-alkyl oximes is to warm them with dilute hydrochloric acid. In this way they yield the carbonyl derivative and O-alkylhydroxylammonium chloride.? The reverse reaction of forming O-alkyl oxime hydrochlorides from carbonyl derivatives and O-alkylhydroxylammonium chlorides is indicated by some of the experiments described in this paper. In addition it was found that a solution of 0-methylacetoxime hydrochloride in dilute alcohol gave a faint test for acetone. The formation of ammonium chloride, therefore, probably depends upon the reduction of the O-alkylhydroxylammonium chloride. This has been shown to proceed quite readily, according to the equation

$$\text{RONH}_2\text{·HCl} + \text{H}_2 \xrightarrow{\text{Pt}} \text{ROH} + \text{NH}_4\text{Cl}$$

The relative amounts of ammonium chloride and O,N-dialkylhydroxylammonium chloride formed evidently might then depend in the main upon three factors: first, the percentage of the products of hydrolysis which are present at equilibrium, second, the relative ease of reduction of the O-alkylhydroxylammonium chloride and the O-alkyl oxime hydrochloride and, third, the readiness with which the system comes to equilibrium when one or more of its products are removed. The first factor mentioned must play *a* very unimportant role, since it was found that in

[7] Dunstan and Goulding, J. *Chem. Soc.*, 79, 631, 635 (1901).

the case of O-methylacetoxime hydrochloride the percentage of the carbonyl derivative in the solution at equilibrium was very small. It was also established that O-methylhydroxylammonium chloride was reduced more rapidly than any of the oximes investigated. However, it was found that, among themselves, the rate at which the oximes absorbed hydrogen varied considerably, being relatively rapid for O-methyl-diethylketoxime and slow for O-methylacetoxime, O-ethylacetoxime and O-methyl-dipropylketoxime. Another difference in the various oximes which must affect the relative amounts of ammonium chloride and O,N-dialkylhydroxylammonium chloride formed is the third factor previously mentioned, namely, the ease with which the equilibrium is reestablished after it has been disturbed. The greater general chemical activity of acetaldehyde and acetone than that of the higher ketones is in harmony with this explanation of the relatively larger amounts of ammonium chloride formed in the reduction of the substituted oximes of acetaldehyde and acetone than those of diethyl ketone and dipropyl ketone.[8]

When a solution of O-methylbenzaldoxime in dilute alcohol containing one equivalent of hydrogen chloride was reduced in the same way with one mole of hydrogen, no hydroxylamine was found among the products of reduction but instead the hydrochlorides of benzyl- and dibenzylamine and considerable unchanged O-methylbenzaldoxime were identified. These results may be represented by the following set of equations

$$C_6H_5CH{=}NOCH_3 + HCl + H_2 \xrightarrow{Pt} (C_6H_5CH_2\overset{H}{N}OCH_3{\cdot}HCl) \xrightarrow{H_2} C_6H_5CH_2NH_2{\cdot}HCl + CH_3OH$$

$$C_6H_5CH{=}NOCH_3 + HCl + H_2O \leftrightarrows C_6H_5CH{=}O + CH_3ONH_2{\cdot}HCl$$

$$C_6H_5CH{=}O + C_6H_5CH_2NH_2{\cdot}HCl \leftrightarrows C_6H_5CH{=}NCH_2C_6H_5{\cdot}HCl \xrightarrow{H_2} (C_6H_5CH_2)_2NH{\cdot}HCl$$

$$CH_3ONH_2.HCl + H_2 \xrightarrow{Pt} CH_3OH + NH_4Cl$$

In support of a mechanism of the formation of benzylammonium chloride which involves the intermediate formation of O-methyl-N-benzylhydroxylammonium chloride it may be noted that Vavon suggested, in connection with the reduction of oximes, that the protection afforded by hydrochloric acid against further reduction to an amine of the first formed hydroxylamine becomes less as the basicity of the hydroxylamine becomes smaller.[4] It is very probable that O-methyl-N-benzylhydroxylamine would be a much weaker base than any of the hydroxylamines that we have previously mentioned.

In a somewhat similar manner a solution of O-ethylacetaldoxime in acetic anhydride was reduced to ethyl acetate and ethyl acetamide, according to the equation

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[8] Stewart, *J. Chem. Soc.*, 87, 185, 410 (1905).

$$CH_3CH{=}NOC_2H_5 + 2(CH_3CO)_2O + 2H_2 \xrightarrow{Pt} CH_3CH_2NH{—}CO{—}CH_3 + CH_3COOC_2H_5 + 2CH_3COOH$$

Experimental Part

Reduction of O-Alkylald- and Ketoxime Hydrochlorides. Method I.—One-fifth of a mole of the carbonyl derivative was added to a solution which had been made by adding the calculated amount of 5 *N* hydrochloric acid to 0.2 of a mole of O-methylhydroxylamine (Eastman Kodak Company) in 150 cc of alcohol. After this solution had been stirred and had stood for an hour, it was catalytically reduced by shaking it with hydrogen in an Adams reduction apparatus, using a pressure of 1 to 3 atmospheres of hydrogen. About 0.2 g. of a platinum catalyst was used, which was prepared by reducing with hydrogen a platinum oxide catalyst which was made according to the method of Adams and Shriner.[9] When necessary, in order to complete the reduction, more of the same catalyst was added to the solution which was being reduced. After the calculated amount of hydrogen had been absorbed, the platinum was removed by filtration and then the alcohol and nearly all of the water was evaporated on a water-bath.

Investigation of the Products Formed in the Reduction of 0-Methyl, Diethyl- and Dipropyl-ketoxime Hydrochlorides.—After the residue left from evaporating the reduced solution had been cooled it was found to consist partly of an oil and partly of a solid. Absolute alcohol was added to a little of the solid portion. That part of the solid which did not dissolve was washed with more alcohol and dried. It was shown to be ammonium chloride by its behavior on being heated, by the fact that its solution in water gave a test for the chloride ion, also that with alkalies a strong odor of ammonia was released and fourth that when benzoyl choride was shaken with an aqueous solution of it to which alkali had been added, a white solid separated, m. p. 128°, which did not lower the melting point of benzamide, m. p. 128°, when the two were mixed.[10]

The rest of the residue from which the alcohol and water had been evaporated was treated with somewhat more than the calculated amount of caustic soda. An oil was extracted from the alkaline solution with ether. The ethereal solution was dried with anhydrous sodium sulfate and then fractionated.

The O-methyl-N-alkylhydroxylamines were colorless oils, which possessed a peculiar terpene-like odor. They were readily soluble in alcohol, ether and ligroin but only slightly soluble in water.

TABLE I

ANALYTICAL AND OTHER DATA

Substituted hydroxylamine	Catalyst, g.	Time of reduction, hours	B. p., °C.	Yield, %	Nitrogen, %	
					Calcd.	Found
$(C_2H_5)_2CH{\cdot}NHOCH_3$	0.2	7	124	48	11.96	11.97
$(C_3H_7)_2CH{\cdot}NHOCH_3$	.6	44	164–166 or 88–89° at 60 mm.	38	9.64	9.68

O-Alkylacetoxime Hydrochloride.—The residue that remained when the reduced solution was evaporated was partly solid and partly an oil. A little of the solid portion was isolated and found to be ammonium chloride. It was possible to isolate in this process a yield of 70 to 80% of ammonium chloride.

In order to isolate the substituted hydroxylamine, the rest of the solid-oil residue mentioned above was made alkaline with concentrated potassium hydroxide and the

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[9] Adams and Shriner, THIS JOURNAL, 45, 2171 (1923).

[10] Schiff and Tassenari, *Ber.*, 10, 1785 (1877).

free base condensed after water had been removed from it by passing the vapors through solid pieces of potassium hydroxide kept at a temperature of 97°. In order to remove dissolved ammonia air was blown for a short time through the liquid which condensed. It was then redistilled. The substituted hydroxylamines obtained were clear, colorless liquids. O-Methyl-*iso*propylhydroxylamine had a terpene-like odor, but it was not as pronounced as was that of O-methyl-N-amyl-3-hydroxylamine. However, O-ethyl-N-isopropylhydroxylamine had an odor more like ethylamine.

TABLE II

ANALYTICAL AND OTHER DATA

Substituted hydroxylamine	Moles of oxime reduced	Catalyst, g.	Time of reduction, hours	B. p., °C.	Yield, %	Nitrogen, % Calcd	Nitrogen, % Found
$(CH_3)_2CHNHOCH$	0.2	0.6	40	76	17	15.72	16.06
$(CH_3)_2CHNHOC_2H_5$	.05	.4	20	78[a]	4	...	...

[a] Hecker, Am. Chem. J., 50, 455 (1913), gives 78° as the b. p

O-Methylacetaldoxime Hydrochloride.—The reduction of 0.2 of a mole of O-methylacetaldoxime hydrochloride in the presence of 0.2 g. of platinum catalyst required four hours. Evaporation of the reduced solution left almost pure ammonium chloride, which was identified in the manner previously described.

O-Methylbenzaldoxime in a Solution of Hydrogen Chloride in Dilute Alcohol.—The reduction of 0.1 of a mole of O-methylbenzaldoxime in 0.1 of a mole of hydrogen chloride in dilute alcohol in the presence of two successively added portions of 0.2 g. of the platinum catalyst required forty-five hours. The reduced solution was concentrated on a water-bath until precipitation started. A white solid appeared when it was cooled, which was filtered off and recrystallized from hot butanol; m. p. 263" corr.;[11] yield, 1.2 g. A test for the chloride ion with silver nitrate was positive. It was only slightly soluble in benzene and ether but more readily soluble in water and alcohol. *Anal.* Calcd. for $(C_6H_5CH_2)_2NH\ HCl$: Cl, 15.20. Found: Cl, 15.20. In order to establish the identity of this hydrochloride more completely, its base was isolated by means of alkali, this solution extracted with ether and the ether solution dried with sodium sulfate. An oil was left, when the ether was distilled, which was dissolved in alcohol. Approximately the calculated amount of phenyl isothiocyanate was then added and the solution was warmed for a few minutes. After it had been cooled a white solid was precipitated from it by the addition of petroleum ether; m. p. 145–146°. It possessed all of the properties ascribed by Dixon[12] to α-phenyl-β,β-dibenzylthiourea.

Water was added to the filtrate from which the above-mentioned hydrochloride, m. p. 263°, was removed. An oil separated which was extracted with ether; the ether solution was dried with anhydrous sodium sulfate and then fractionally distilled. After the ether had passed over, all of the oil that remained, aside from a very small amount of a very high-boiling liquid which was unidentified, distilled from 187–194°; yield 2 g. Since this liquid was insoluble in water and dilute acid and since its boiling point was about that of O-methylbenzaldoxime, which boils at 191°,[13] it seemed probable that it was this substituted oxime. In order to hydrolyze it a portion of this liquid was accordingly dissolved in concentrated hydrochloric acid. As it stood at room temperature an oil gradually separated which had the odor of benzaldehyde. After a day this

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[11] Limpricht, Am., 144, 314 (1867), gives 256° (probably uncorrected) as the m. p. of dibenzylammonium chloride.

[12] Dixon, *J.* Chem. Soc., 63, 539 (1893).

[13] Traube, *Ber.*, 53, 1486 (1920).

oil was extracted with ether. A solution of *p*-nitrophenylhydrazine hydrochloride in water was shaken for several minutes with this ether solution. Evaporation of the ether left a reddish-brown solid, which was recrystallized from alcohol; m. p. 193°.[14] The aqueous solution from which the benzaldehyde was extracted was evaporated to dryness on a water-bath. A white solid remained which was recrystallized by dissolving it in absolute alcohol and reprecipitating it with dry ether; m. p. 148°.[15] When alkali was added to this hydrochloride the characteristic odor of O-methylhydroxylamine was noted.

The aqueous solution from which the O-methylbenzaldoxime was extracted was made alkaline with caustic soda. An oil separated which was extracted with ether. After the ether solution had been dried with sodium sulfate it was fractionated. An oil which boiled at 184–185° was obtained; yield. 1 g.[16] To a solution of a small amount of this oil in benzene was added the calculated amount of phenyl isocyanate. After this solution had stood overnight a white solid was found, which was recrystallized from alcohol; m. p. 170–171°. α-Phenyl-β-benzylurea made from benzyl isocyanate and aniline according to the method of Letts[17] also melted at 170–171°. In addition, a mixture of these two solids melted at 170–171°, which indicates that the liquid which boiled at 184–185° was benzylamine.

Method II

Preparation of O-Methylketoximes, $R_2C{=}NOCH_3$.—To 0.2 of a mole of O-methylhydroxylamine was added 0.2 of a mole of the ketone. After the solution had stood for four days anhydrous calcium chloride was added to it to absorb water. The unabsorbed oil was decanted, again dried with calcium chloride and fractionated. O-Methylacetoxime boiled at 72–74°;[18] yield, 20%. O-Methyldiethylketoxime distilled at 116–117°; yield, 66%. It was readily soluble in alcohol, ether and ligroin but insoluble in water.

Anal. Calcd. for $C_6H_{13}ON$: N, 12.17. Found: N, 12.36.

Reduction of O-Methylketoxime Hydrochlorides.—The calculated amount of 4 N hydrochloric acid necessary to neutralize it was added to the O-methylketoxime and then sufficient alcohol was added in order to unite the two liquid layers which were at first present. The solution was reduced in the manner described previously for the reduction of the O-methyldialkylketoxime hydrochlorides prepared by the other method

Ammonia and O-methyl-N-amyl-3-hydroxylamine, b. p. 124°, with its characteristic terpene-like odor were obtained from the reduction products of O-methyldiethylketoxime hydrochloride in the same way as was described previously.

When the reduction of the 0-methylacetoxime hydrochloride was complete the solution gave a distinct qualitative test for methyl alcohol with guaiacol sulfate,[19] and for acetone with sodium nitroprusside.[20] The presence of acetone was also proved

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[14] Rosenthaler, "Der Nachweis organischer Verbindungen," Verlag von Ferdinand Enke, Stuttgart, 1914, p. 132, gives 192–193° as the m. p. of benzaldehyde-*p*-nitrophenylhydrazone.

[15] Lossen, *Ber.*, 16, 827 (1883), gives 149° as the m. p. of O-methylhydroxylammonium chloride.

[16] According to "International Critical Tables," McGraw-Hill Book Co., New York, 1926, Vol. I, p. 211, the b. p. of benzylamine is 184°.

[17] Letts, *Ber.*, 5, 93 (1872).

[18] Ponzio and Charrier, *Gazz. chim. ital.*, I, 37, 506 (1907), give 73° as the b. p.

[19] "Deutsches Arzneibuch," Decker's Verlag, Berlin, 1926, p. LIV.

[20] Gadamer, "Lehrbuch der chemischen Toxicologie," Vanderhoeck and Ruprecht, Göttingen, 1924, p. 308.

by the formation of its *p*-nitrophenylhydrazone when p-nitrophenylhydrazine hydrochloride was added to the solution which had been reduced. It melted at 149" and did not lower the melting point of acetone-p-nitrophenylhydrazone; m. p. 149°.[21] When the reduced solution was evaporated, a white solid and a small amount of oil were obtained. The solid portion was proved to be ammonium chloride by tests which have been mentioned previously.

α-Phenyl-*β*-methoxy-*β*-amyl-3-thiourea, $C_6H_5NHCS{\cdot}N(OCH_3){\cdot}CH(C_2H_5)_2$.—To a solution of 2.7 g. (0.02 mole) of phenyl isothiocyanate in benzene was added 2.4 g. (0.02 mole) of O-methyl-N-amyl-3-hydroxylamine, which was obtained from the reduction products of O-methyldiethylketoxime hydrochloride. After the solution thus formed had stood at room temperature for a day the benzene was evaporated. A white solid remained which was recrystallized from 50% alcohol; m. p. 57". It was soluble in alcohol, benzene and ligroin, but insoluble in water.

Anal. Calcd. for $C_{13}H_{20}ON_2S$: N, 11.11. Found: 11.61.

Reduction of O-Methylhydroxylammonium Chloride.—The calculated amount of 4 N hydrochloric acid was added to 0.2 of a mole of 0-methylhydroxylamine. It was reduced in one hour by hydrogen in the presence of 0.2 g. of the platinum catalyst in the usual manner. The solution which had been reduced gave a strong test for methanol with guaiacol sulfate.[19] Ammonium chloride was left as a residue when the reduced solution was evaporated to dryness. It was identified in the same way as was the ammonium chloride formed in the reduction of the O-alkylacetoxime hydrochlorides which has been previously described.

Partial Hydrolysis of 0-Methylacetoxime Hydrochloride.—A solution prepared by mixing equivalent proportions of O-methylhydroxylamine, hydrochloric acid and acetone in dilute alcohol. in the same way as was that prepared for reduction, was allowed to stand for half an hour. At the end of this time it was tested for acetone with sodium nitroprusside.[20] The depth of color produced in this test was compared with the color produced in standard solutions of acetone in dilute alcohol which were treated in the same way. By such comparisons it was found that the solution being tested contained a little acetone but that the amount was less than 5% of that originally added. However, when it was heated rapidly, cooled and then retested, the percentage of acetone was considerably higher for a short time.

Reduction of O-Ethylacetaldoxime in Acetic Anhydride.—A solution of 3.4 g. of O-ethylacetaldoxime in 10 cc. of acetic anhydride was reduced with hydrogen in the usual way in the presence of 0.2 g. of platinum catalyst. Somewhat more than one molecular equivalent of hydrogen was absorbed in fifty minutes. When the reaction bottle was opened at the end of the experiment, the odor of ethyl acetate was quite pronounced. In order to hydrolyze the solution it was refluxed for an hour with a solution of 20 g. of potassium hydroxide in 40 cc. of 50% alcohol and then the volatile portion distilled into dilute hydrochloric acid. This acid solution was evaporated almost to dryness on a water-bath. A concentrated solution of potassium hydroxide was added to the residue and the free base which was released was condensed after it had been passed through solid potassium hydroxide at 97°. When it was redistilled it boiled under 25". A white solid formed when it was shaken with ethyl oxalate, m. p. 181°. The melting point was not changed when it was mixed with diethyloxamide.[22]

O-Methyl-N-Alkylhydroxylamines from O-Methyl-N-Substituted Hydroxyurethans

Preparation of O-Alkylhydroxyurethan, $RONHCOOC_2H_5$.—O-Methyl- and O-ethyl-hydroxyurethans were prepared by a modification of the method used by Major

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[21] Bamberger and Sternitzki, *Ber.*, 26, 1306 (1893).

[22] Schiff, *ibid.*, 17, 1034 (1884), gives 179" as the m. p. of diethyloxamide.

and Fleck[23] to prepare O,N-dialkylhydroxyurethans and small amounts of O-alkylhydroxyurethans. In order to increase the amount of O-alkylhydroxyurethan, only 2.1 moles of dialkyl sulfate and 600 cc. of a 20% solution of potassium hydroxide were used instead of the 4.25 moles of the former and the 3200 cc of the latter which were used by these investigators. Otherwise the preparation of the O-alkylhydroxyurethans was carried out as it is described by these authors: O-methylhydroxyurethan, yield, 29%, b. p. 186–188°; O-ethylhydroxyurethan, yield, 43%, b. p. 195–196°.

Preparation of **O-Methyl-N-alkylhydroxyurethan, $CH_3ONRCOOC_2H_5$.**—One molecular equivalent of sodium dissolved in absolute methanol was added to a solution of one molecular equivalent each of O-methylhydroxyurethan and of alkyl iodide. After this mixture had been well shaken and had stood at room temperature for a day a rather large white precipitate had formed. In order to complete the reaction the mixture was refluxed for five hours. At the end of this time most of the methanol was distilled off and water was added to the residue in order to dissolve the white solid. This aqueous solution was then extracted repeatedly with ether. Then, in order to remove unchanged O-methylhydroxyurethan, the ether solution was in turn extracted several times with a dilute solution of sodium hydroxide. The ether solution was dried with anhydrous sodium sulfate, the ether distilled and the oil that remained was fractionated. O-Methyl-N-*iso*propylhydroxyurethan boiled at 164–167° (at 734 mm.); yield, 49% (31 g.). O-Methyl-N-amyl-3-hydroxyurethan boiled at 196°; yield, 16% (3 g.).

Anal. Calcd. for $C_7H_{15}O_3N$: N, 8.70. Found: N, 9.22. Calcd. for $C_9H_{19}O_3N$: N, 7.41. Found: N, 8.09.

Preparation of **O-Methyl-N-*iso*propylhydroxylamine, $(CH_3)_2CH{\cdot}NHOCH_3$.**—A solution of 0.125 mole of O-methyl-N-*iso*propylhydroxyurethan in 50% alcohol containing 0.475 mole of potassium hydroxide was refluxed for three hours. The volatile portion was then distilled into dilute hydrochloric acid. This acid solution was evaporated to dryness on a water-bath. An oily hydrochloride was left as a residue, from which the free base was obtained by warming it with potassium hydroxide. The vapors which formed were passed through solid potassium hydroxide at a temperature of 97°. Redistillation gave a light liquid with a terpene-like odor; b. p. 75–76°; yield, 60%.

Preparation of **O-Methyl-N-amyl-3-hydroxylamine, $(C_2H_5)_2CHNHOCH_3$.**—A solution of 2.4 g. (0.013 mole) of O-methyl-N-amyl-3-hydroxyurethan in 50% alcohol containing 3 molecular equivalents of potassium hydroxide was refluxed for four hours. The volatile portion was then distilled into dilute hydrochloric acid. This acid solution was evaporated to dryness on a water-bath. Sufficient cold caustic soda to more than combine with all of the chloride ion was added to this residue. Then the alkaline solution was extracted with ether, the ether solution was dried with sodium sulfate and then fractionally distilled. After the ether had been distilled, an oil remained which boiled at 124" and possessed the characteristic terpene-like odor of O-methyl-N-amyl-3-hydroxylamine; yield, 32%.

Chloroplatinates of **O-Alkyl-N-alkylhydroxylamines.**—Somewhat more than the calculated amount of hydrogen chloride was passed into a solution of the O-alkyl-N-alkylhydroxylamine in absolute alcohol. To this solution was added the calculated amount of a concentrated solution of chloroplatinic acid in absolute alcohol. When dry ether was added an orange-colored precipitate formed. In order to purify it, it was redissolved in absolute alcohol and reprecipitated with dry ether in the form of orange-yellow colored needles.[24]

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[23] Major and Fleck, THIS JOURNAL, 50, 1479 (1928).

[24] It was necessary to fractionally precipitate the chloroplatinate formed from the O-methyl-N-isopropylhydroxylamine which was obtained when O-methylacetoxime

TABLE III

CHLOROPLATINATES OF THE O-METHYL-N-ALKYLHYDROXYLAMINES WHICH WERE FORMED BY THE HYDROLYSIS OP O-METHYL-N-ALKYLHYDROXYURETHANS

Substituted hydroxylamine	M. p., °C. with dec.	Platinum, % Calcd.	Pound
O-Methyl-N-*iso*propyl-	183	33.19	32.93
O-Methyl-N-amyl-3-	161	30.30	30.10

TABLE IV

CHLOROPLATINATES OF THE O-ALKYL-N-ALKYLHYDROXYLAMINES WHICH WERE OBTAINED FROM THE REDUCTION PRODUCTS OF O-ALKYLKETOXIME HYDROCHLORIDES

Substituted hydroxylamine	M. p., °C. with dec.	Platinum, % Calcd.	Found
O-Methyl-N-*iso*propyl-	183[a]	33.19	32.74
O-Ethyl-N-*iso*propyl-	174	31.68	31.65
O-Methyl-N-amyl-3-	161[b]	30.30	30.54

[a] A mixture of the chloroplatinates of the O-methyl-N-*iso*propylhydroxylamine which was obtained from the reduction product of O-methvlacetoxime hvdrochloride and of that formed in the hydrolysis of O-methyl-N-*iso*propylhydroxyurethan also melted with decomposition at 183°.

[b] A mixture of the chloroplatinate which was obtained from the reduction product of O-methyldiethylketoxime hydrochloride and that formed in the hydrolysis of O-methyl-N-amyl-3-hydroxyurethan also melted with decomposition at 161°.

α-Phenyl-β-methoxy-β-alkylureas, $C_6H_5NHCONROCH_3$.—α-Phenyl-β-methoxy-β-amyl-3-urea was prepared by letting a solution of equimolecular proportions of O-methyl-N-amyl-3-hydroxylamine and phenyl isocyanate in benzene stand for five hours. When the benzene was evaporated, an oil remained as a residue, which solidified after it had stood overnight in a vacuum desiccator. In order to purify it, it was dissolved in freshly distilled petroleum ether, extracted with dilute hydrochloric acid and then the petroleum ether was evaporated. The solid was dried in a vacuum desiccator containing sulfuric acid and solid potassium hydroxide. It was readily soluble in all ordinary organic solvents but insoluble in water.

The other α-phenyl-β-methoxy-β-alkylureas were formed when a solution of equimolecular proportions of the O-methyl-N-alkylhydroxylamine and phenyl isocyanate in petroleum ether had stood for an hour. The white solid precipitated from the petroleum ether was recrystallized from hot ligroin.

The α-phenyl-β-methoxy-β-*iso*propylurea which was made from the O-methyl-N-*iso*propylhydroxylamine that had been obtained from O-methyl-N-isopropylhydroxyurethan melted at 73°.

Anal. Calcd. for $C_{11}H_{16}O_2N_2$: N, 13.46. Found: N, 13.79.

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hydrochloride was reduced. The first portion of the precipitate which formed when ether was added to the solution of the chloroplatinate in alcohol did not melt sharply and analysis revealed that it contained a lower percentage of platinum than that calculated for O-methyl-N-*iso*propylhydroxylamine chloroplatinate. The larger fraction of the chloroplatinate which was precipitated when more ether was added to the filtrate melted sharply and as may be seen from the following table it yielded, within the experimental error the calculated percentage of platinum for the chloroplatinate of O-methyl-N-*iso*propylhydroxylamine. The fraction which first precipitated probably contained a very small amount of ammonium chloride. This was probably formed due to the presence of a small amount of dissolved ammonia in the O-methyl-N-*iso*propylhydroxylarnine.

TABLE V

α-PHENYL-β-METHOXY-β-ALKYLUREAS THAT WERE FORMED FROM THE O-METHYL-N-ALKYL-HYDROXYLAMINES WHICH HAD BEEN OBTAINED FROM THE REDUCTION PRODUCT OF O-METHYLKETOXIME HYDROCHLORIDES

Alkyl group	M. p., °C.	Nitrogen, %	
		Calcd.	Found
Isopropyl-	73[a]	13.46	13.43
Amyl-3-	59	11.86	12.11
Heptyl-4-	109	10.41	10.74

[a] A mixture of the α-phenyl-β-methoxy-β-*iso*propylureas that were obtained from the O-methyl-N-*iso*propylhydroxylamine formed from the reduction product of O-methylacetoxime hydrochloride and that which was formed from O-methyl-N-*iso*propyl-hydroxyurethan also melted at 73°.

Summary

1. Several O-alkylketoxime hydrochlorides have been catalytically reduced in dilute alcohol to O-alkyl-N-alkylhydroxylamine hydrochlorides, ammonium chloride and other products. The mechanism of the formation of these compounds has been discussed.

2. The corresponding O-alkyl-N-alkylhydroxylamines have been synthesized by the hydrolysis of O-alkyl-N-alkylhydroxyurethans, which were made by the action of alkyl iodides on O-alkyl-hydroxyurethans in the presence of sodium methylate.

3. A number of derivatives of these substituted hydroxylamines have been prepared.

4. The only nitrogen-containing compound that was isolated when O-methylacetaldoxime hydrochloride was catalytically reduced was ammonium chloride, but when O-ethylacetaldoxime dissolved in acetic anhydride was reduced, ethyl acetate and ethyl acetamide were obtained.

5. When O-methylbenzaldoxime was catalytically reduced in a solution of hydrogen chloride in dilute alcohol, benzyl- and dibenzylammonium chlorides were formed. The mechanism of the formation of these compounds has been discussed.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF MCLAUGHLIN GORMLEY KING COMPANY]

STUDIES ON PYRETHRUM FLOWERS. II. THE RELATION BETWEEN MATURITY AND PYRETHRIN CONTENT

BY C. B. GNADINGER AND C. S. CORL

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Handlers of *Pyrethrum* flowers have quite generally held the opinion that the immature or closed flowers have greater insecticidal power than open or mature flowers. So firmly fixed has this idea become, that closed Dalmatian flowers command a premium of five to six cents a pound over half-closed flowers, which in turn, cost two to three cents a pound more than open flowers. At the present time, Dalmatian open flowers are slightly higher in price than Japanese flowers, which are not graded as closed and open.

In a previous paper[1] the writers described a method for determining the percentage of active principles in *Pyrethrum* flowers. By the application of this method to flowers in different stages of maturity, it has been possible to determine the comparative value of open and closed flowers.

Experimental Part

Difficulty was experienced in obtaining suitable material, because *Pyrethrum* flowers are not grown commercially in the United States. Through the courtesy of Mr. E. B. Fischer of the College of Pharmacy, University of Minnesota, a plot of *Pyrethrum roseum* was made available for this work. Samples were collected from these plants, which were three to five years old, at intervals throughout the flowering season, and the flowers were carefully shade dried. The analyses of the samples are presented in Table I.

Before the buds were formed, the roots, leaves and stems did not contain any pyrethrins. As the buds formed and developed, their pyrethrin content gradually increased. The last and most mature sample contained four times the percentage of pyrethrins found in the unexpanded buds. Samples four and six represented closed flowers at the same stage of development but collected at different times; sample six contained considerably more active material than number four, indicating that the pyrethrin content depends on the maturity of the plant as well as on the development of the flowers. The average weight of the open flowers was two to three times that of the closed flowers, and the pyrethrin content of the former was about double that of the closed flowers. Therefore, the yield of pyrethrins from a given unit of land can be approximately quadrupled by merely allowing the flowers to mature.

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[1] Gnadinger and Corl, THIS JOURNAL, 51,3054 (1929).

TABLE I

ANALYSES OF PYRETHRUM ROSEUM AT DIFFERENT STAGES OF MATURITY

Date collected	No.	Description
May 7	1	Roots
May 7	2	Entire plant except roots; buds extremely small
May 23	3	Unexpanded buds; ray florets not showing
May 30	4	Closed flowers; ray florets visible but not expanded
June 5	5	Half-open flowers; disk florets visible; ray florets partly expanded
June 11	6	Closed flowers; same description as No. 4
June 11	7	Open flowers; ray florets completely expanded; disk florets partly expanded
June 21	8	Open flowers; ray florets expanded; disk florets expanded
June 28	9	Open flowers; completely expanded; last of crop

No.	Av. wt., g. Fresh	Av. wt., g. Dried	Diam., mm Fresh	Diam., mm Dried	Moisture in dry flowers, %	Pyrethrins (dry-basis), %
1	....	..	..	..	...	None
2	..	..	..	..	...	None
3	0.138	0.023	5–10	3– 7	4.6	0.22
4	.304	.052	6–13	4– 9	5.6	.40
5	.391	.086	6–14	5–11	4.9	.54
6	.285	.057	6–11	4– 9	4.9	.56
7	.502	.106	6–15	5–12	6.0	.67
8	.675	.154	9–20	7–15	6.0	.78
9	.400	.096	8–16	6–12	10.0	.87

Growing plants were not available for similar work on *Pyrethrum cinerariaefolium*, but five samples of flowers of known origin were examined in the following manner: each sample was thoroughly mixed and the

TABLE II

COMPARATIVE PYRETHRIN CONTENT OF OPEN AND CLOSED FLOWERS (*Pyrethrum cinerariaefolium*)

No.	Kind of flowers	Part of sample analyzed	Diam. of flowers, mm.	Av. wt. of flowers, g.
20	Japanese	Original sample	..	..
20	Japanese	Closed flowers	6–9	0.109
20	Japanese	Open flowers	9–15	.208
25	Japanese	Original sample	..	..
25	Japanese	Closed flowers	4–9	.101
25	Japanese	Half-closed flowers	8–12	.193
25	Japanese	Open flowers	11–14	.238
23	Dalmatian	Original sample	..	..
23	Dalmatian	Closed flowers	4–8	.064
23	Dalmatian	Open flowers	8–12	.143
24	Dalmatian	Original sample	..	..
24	Dalmatian	Closed flowers	5–8	.074
24	Dalmatian	Open flowers	10–14	.178
26	American	Original sample	..	..
26	American	Closed flowers	6–8	,086
26	American	Open flowers	9–15	.135

TABLE II (*Concluded*)

No.	Composition of original sample, %: Closed	Half-closed	Open	Stems	Debris	Pyrethrin content, %	Ratio pyrethrin content closed:open
20	9.8	20.0	64.0	0.4	5.8	0.96	
20	..	...	..	0.0	0.0	.80	
20	..	..	..	0.0	0.0	.94	1:1.18
25	36.0	40.0	16.0	1.2	6.8	.84	
25	..	...	..	0.0	0.0	.76	
25	..	...	..	0.0	0.0	.95	
25	..	...	..	0.0	0.0	.97	1:1.28
23	68.4	16.0	12.1	0.7	2.8	.53	
23	..	...	..	0.0	0.0	.61	
23	..	...	..	0.0	0.0	.81	1:1.32
24	53.2	24.4	16.6	2.1	3.7	.52	
24	..	...	..	0.0	0.0	.48	
24	..	...	..	0.0	0.0	.71	1:1.48
26	26.4	17.5	52.4	2.9	0.8	.85	
26	..	...	..	0.0	0.0	.64	
26	..	...	..	0.0	0.0	1.03	1:1.61

percentage of closed, half-closed and open flowers was determined. A portion of the original sample was then ground and analyzed. From the remainder of the original sample, the closed and open flowers were carefully separated, selecting only complete flowers and rejecting those from which parts were missing. The pyrethrin content of the closed and open flowers was determined. The results obtained are compared in Table II.

The open flowers contained from 18 to 61% more active principle than the closed flowers from the same lots.

It is well known that certain parts of the Pyrethrum flower-head contain more active principle than others,[2] but the distribution of the pyrethrins in the different flower parts has not been determined accurately heretofore. A sample of uncompressed Japanese flowers was carefully separated into the principal parts, using for this purpose flowers from which none of the parts were missing. The analyses of these parts are given in Table III.

TABLE III

DISTRIBUTION OF ACTIVE PRINCIPLE IN JAPANESE PYRETHRUM CINERARIAEFOLIUM

Sample No. 25	Composition of flowers, %	Pyrethrins, %	Percentage of total pyrethrins
Achenes	34.2	2.27	92.4
Receptacles	11.3	0.26	3.5
Involucral scales	11.5	0.15	2.0
Disk florets	25.8	Trace	..
Ray florets	17.2	Trace	..
Original sample	..	0.84	..
Stems	..	0.15	..

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[2] U. S. Dept. Agr., "Insect Powder," Bulletin 824 revised, 1926.

The achenes contained 92.4% of the total pyrethrins; the receptacles and scales contained 3.5 and 2.0%, respectively, while the disk and ray florets contained mere traces. Analysis of the original sample showed 0.84% of pyrethrins, while calculation of the total pyrethrin content from the analyses of the parts gave a pyrethrin content of 0.82%. It would seem, therefore, that a high pyrethrin content depends on the development of the achenes.

The fact that the receptacles and scales and other outer parts of the flower-head contain only a small proportion of pyrethrins is of some importance. Should an attempt be made to increase the apparent pyrethrin content, obtained by the use of the method,' by coating or spraying flowers with a petroleum-ether soluble, copper reducing material, the adulteration could be detected by the high pyrethrin content of the outer parts of the flower. This is apparent from Table IV, in which the pyrethrin content of the outer parts of five samples of flowers is reported.

TABLE IV

PYRETHRIN CONTENT OF RECEPTACLES AND INVOLUCRAL SCALES

No.	Rind of flowers	Pyrethrins, in recept.,[a] %	Recept.[a] in flowers, %	Percentage of total pyrethrins in recept.[a]	Pyrethrins in orig. flowers, %
20	Japanese	0.27	25.0	7.0	0.96
25	Japanese	.20	22.8	5.4	.84
25	Japanese (closed)	.26	30.8	10.5	.76
23	Dalmatian	.17	31.1	10.0	.53
24	Dalmatian	.17	30.0	9.8	.52

"Scales included.

Summary

Contrary to popular belief, the pyrethrin content increases as the flowers mature, so that open flowers contain more active principle than closed flowers from the same plants. There is also some evidence that the earlier flowers produced contain less pyrethrins than the later flowers but this was not proved conclusively. Open flowers from commercial samples contained from 18 to 61% more active principle than closed flowers from the same lots.

The average weight of the open flowers is about double that of closed flowers. Therefore, the pyrethrins produced from a given tract of land can be increased three to four times by merely allowing the flowers to mature.

The roots, stems and leaves contain no pyrethrins before the flower buds are formed.

In the sample analyzed the achenes contained more than 90% of the active material. The receptacles and involucral scales contained most of the remainder. The disk and ray florets yielded only traces of pyrethrins. The low pyrethrin content of the outer parts of the flower is important because it affords a means for detecting certain types of adulteration.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF MCLAUGHLIN GORMLEY KING COMPANY]

STUDIES ON PYRETHRUM FLOWERS. III. THE PYRETHRIN CONTENT OF DIFFERENT COMMERCIAL VARIETIES

BY C. B. GNADINGER AND C. S. CORL

RECEIVED JULY 23, 1929 PUBLISHED FEBRUARY 6, 1930

The three species of *Pyrethrum* flowers that have insecticidal value are *Pyrethrum cinerariaefolium, Pyrethrum roseum* and *Pyrethrum carneum;* of these *Pyrethrum cinerariaefolium* is by far the most important. In 1928 more than eleven million pounds of *Pyrethrum cinerariaefolium* were imported into the United States from Europe and Japan, the latter country supplying about five times as much as all other sources combined. The amount of *Pyrethrum roseum* imported is negligible, but it is widely grown in this country for its ornamental flowers. *Pyrethrum carneum* is of no commercial importance.

The two principal commercial varieties of flowers, Dalmatian and Japanese, belong to the species *Pyrethrum cinerariaefolium.* There are several commercial grades of these flowers and it has been shown[1] that the trade preference for certain grades is unwarranted. The purpose of this paper is to show the comparative value of the different commercial varieties of *Pyrethrum* flowers.

Experimental

Twenty-eight commercial samples of whole flowers were collected from dealers in the United States and also from agents in Japan and Europe. Twenty samples of powdered commercial flowers were kindly supplied by Dr. C. C. McDonnell, Chief, Insecticide Control, United States Department of Agriculture. These powders had been kept in air-tight containers for two or three years. Two samples of *Pyrethrum cinerariaefolium* grown in Virginia were obtained through the courtesy of Dr. A. F. Sievers, Senior Biochemist, Bureau of Plant Industry, United States Department of Agriculture. Five samples of Minnesota and Iowa grown *Pyrethrum roseum* were collected and ten samples of ground or powdered commercial lots were obtained from large manufacturers of *Pyrethrum* sprays. Samples of *Pyrethrum carneum* could not be obtained.

The flowers were examined to determine the proportion of closed, half-closed, and open flowers and stems. Some of the Japanese flowers were com-

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[1] Gnadinger and Corl, THIS JOURNAL, 52, 680 (1930).

TABLE I

THE PYRETHRIN CONTENT OF PYRETHRUM FLOWERS

No.	Description *Pyrethrum cinerariaefolium*	Crop, year	Composition of sample, % Closed	Half-closed	Open	Stems	Misc.[a]	Achenes	Receptacles	Disk florets	Ray florets	Moisture, %	Pyrethrins, %
46	Closed Dalmatian, powdered	1926	. .	. .	. .	. . .	1.3	6.5	28.0	43.2	21.0	. . .	0.38
35	Closed Dalmatian, powdered	1925	. .	. .	. .	. . .	4.2	13.0	24.0	34.0	24.8	. . .	.39
42	Closed Dalmatian, powdered	1926	. .	. .	. .	. . .	0.8	6.8	28.9	37.0	26.5	4.0	.39
7	Closed Dalmatian, whole	1928	74.1	14.0	8.9	0.8	1.6	. .	. .	. .	. .	6.2	.40
27	Closed Dalmatian, whole	1928	44.0	22.0	18.0	0.8	15.2	. .	. .	. .	. .	7.0	.40
45	Closed Dalmatian, powdered	1926	. .	. .	. .	. . .	0.8	6.9	28.0	44.4	19.9	4.2	.41
33	Closed Dalmatian, powdered	1926	. .	. .	. .	. . .	1.9	9.9	26.5	38.5	23.2	. . .	.42
13	Closed Dalmatian, whole	1925	. .	. .	. .	. . .	. .	. .	. .	. .	. .	5.9	.44
21	Closed Dalmatian, whole	1925	. .	. .	. .	1.1	. .	. .	. .	. .	. .	. . .	.45
48	Closed Dalmatian, powdered	1926	. .	. .	. .	. . .	1.4	8.4	27.0	42.1	21.1	. . .	.45
24	Closed Dalmatian, whole	1928	53.2	24.4	16.6	2.1	3.7	. .	. .	. .	. .	4.3	.52
14	Closed Dalmatian, whole	1925	. .	. .	. .	. . .	. .	. .	. .	. .	. .	. . .	.53
23	Closed Dalmatian, whole	1928	68.4	16.0	12.1	0.7	2.8	. .	. .	. .	. .	6.0	.53
11	Closed Dalmatian, whole	1925	. .	. .	. .	. . .	. .	. .	. .	. .	. .	. . .	.57
37	Half-closed Dalmatian, powdered	1925	. .	. .	. .	. . .	0.3	34.7	22.0	23.1	19.9	4.0	.38
38	Half-closed Dalmatian, powdered	1926	. .	. .	. .	. . .	0.8	38.5	20.4	22.4	17.9	. . .	.38
47	Half-closed Dalmatian, powdered	1926	. .	. .	. .	. . .	1.9	28.0	20.0	30.6	19.5	4.5	.38
29	Half-closed Dalmatian, whole	1928	15.4	21.5	46.2	1.5	15.4	. .	. .	. .	. .	. . .	.53
4	Half-closed Dalmatian, whole	1927	. .	. .	. .	. . .	. .	. .	. .	. .	. .	. . .	.57
40	Open Dalmatian, powdered	1925	. .	. .	. .	. . .	0.9	47.9	16.4	18.8	16.0	. . .	.39
31	Open Dalmatian, powdered	1925	. .	. .	. .	. . .	. .	52.0	. .	16.6	. .	. . .	.40
50	Open Dalmatian, powdered	1926	. .	. .	. .	. . .	1.5	51.4	18.3	14.0	14.8	5.0	.40
6	Open Dalmatian, whole	1927	. .	. .	. .	. . .	. .	. .	. .	. .	. .	. . .	.43
43	Open Dalmatian, powdered	1926	. .	. .	. .	. . .	1.1	47.4	18.3	13.4	19.8	. . .	.43
16	Open Dalmatian, whole	1925	. .	. .	. .	. . .	. .	. .	. .	. .	. .	. . .	.47
28	Open Dalmatian, whole	1928	5.5	11.0	66.7	0.7	16.1	. .	. .	. .	. .	. . .	.51
36	Open Dalmatian, powdered	1926	. .	. .	. .	. . .	6.4	57.1	18.0	5.5	13.0	. . .	.58
22	Japanese, whole, compressed	1928	. .	. .	. .	. . .	. .	. .	. .	. .	. .	. . .	.58
32	Japanese, powdered, compressed	1925	. .	. .	. .	. . .	. .	. .	. .	. .	. .	. . .	.62
44	Japanese, powdered, compressed	1926	. .	. .	. .	. . .	. .	. .	. .	. .	. .	. . .	.62
39	Japanese, powdered, compressed	1926	. .	. .	. .	. . .	. .	. .	. .	. .	. .	. . .	.64
41	Japanese, powdered, compressed	1926	. .	. .	. .	. . .	. .	. .	. .	. .	. .	. . .	.68
34	Japanese, powdered, compressed	1926	. .	. .	. .	. . .	. .	. .	. .	. .	. .	4.6	.71
49	Japanese, powdered, compressed	1926	. .	. .	. .	. . .	. .	. .	. .	. .	. .	3.9	.74
60	Japanese, whole, compressed	1928	. .	. .	. .	. . .	. .	. .	. .	. .	. .	. . .	.74

TABLE I (*Concluded*)

No.	Description	Crop, year	Composition of sample, %									Moisture. %	Pyrethrins, %
	Pyrethrum cinerariaefolium		Closed	Half-closed	Open	Stems	Misc.[a]	Achenes	Receptacles	Disk florets	Ray florets		
3	Japanese, whole, compressed	1928	..	..	..	...	..	..	..	..	..	...	0.80
61	Japanese, whole, compressed	1928	..	..	..	...	..	..	..	..	..	...	.81
25	Japanese, whole, not compressed	1928	36.0	40.0	16.0	1.2	1.8	34.2	22.8	25.8	17.2	...	.84
30	Japanese, whole, compressed	1928	..	..	..	...	..	..	..	..	..	...	.86
2	Japanese, whole, compressed	1926	..	..	..	...	..	..	..	..	..	5.7	.87
62	Japanese, whole, compressed	1928	..	..	..	...	..	..	..	..	..		.87
56	Japanese, whole, compressed	1928	..	..	..	...	..	..	..	..	..	...	.92
20	Japanese, whole, not compressed	1928	9.8	20.0	64.0	0.4	5.8	..	..	..	..	...	.96
51	Japanese, whole, compressed	1928	..	..	..	...	..	..	..	..	..	6.5	.99
19	Japanese, whole, not compressed	1928	..	..	..	...	..	..	..	..	..	...	1.10
17	Japanese, whole, not compressed	1928	..	..	..	...	..	..	..	..	..	...	1.17
18	Japanese, whole, not compressed	1928	..	..	..	...	..	..	..	..	..	...	1.20
1	Japanese, whole, compressed	1928	..	..	..	...	..	..	..	..	..	...	1.21
26	Half-open American, whole (Virginia)	1928	27.2	18.0	54.0	3.0	0.8	..	..	..	..	...	0.85
58	Half-open American, whole (Virginia)	1929	..	..	..	...	..	..	..	..	..	7.3	1.11
	Pyrethrum roseum												
52	American whole, Minnesota	1929	74.2	25.8	0.0	0.0	0.0	..	..	..	..	...	0.25
59	American whole, Minnesota	1929	0.0	0.0	100	.0	.0	..	..	..	..	...	.56
54	American whole, Minnesota	1929	.0	.0	100	.0	.0	..	..	..	..	6.0	.73
55	American whole, Iowa	1929	.0	.0	100	.0	.0	..	..	..	..	6.6	.79
53	American whole, Minnesota	1929	.0	10.1	89.9	.0	.0	..	..	..	..	8.9	.82
	Commercial lots, unknown origin												
70	Powdered		..	..	..	...	..	..	..	..	..	...	.41
67	Ground		..	..	..	...	..	..	..	..	..	...	.54
68	Powdered		..	..	..	...	..	..	..	..	..	...	.57
65	Ground		..	..	..	...	..	..	..	..	..	...	.58
5	Ground		..	..	..	...	..	..	..	..	..	...	.59
66	Ground		..	..	..	...	..	..	..	..	..	...	.66
57	Ground		..	..	..	...	..	..	..	..	..	...	.68
63	Ground		..	..	..	...	..	..	..	..	..	...	.72
69	Powdered		..	..	..	...	..	..	..	..	..	...	.72
64	Ground		..	..	..	...	..	..	..	..	..	...	.79

[a] Parts of flowers, principally.

TABLE II

SUMMARY OF ANALYSES OF PYRETHRUM FLOWERS

Samples analyzed	Species	Description	Pyrethrin content, % Minimum	Maximum	Average
14	*Cinerariaefolium*	Dalmatian closed	0.38	0.57	0.448
5	*Cinerariaefolium*	Dalmatian half-closed	.38	.57	.448
8	*Cinerariaefolium*	Dalmatian open	.39	.58	.451
27	*Cinerariaefolium*	Dalmatian, all grades	.38	.58	.449
21	*Cinerariaefolium*	Japanese	.58	1.21	.853
2	*Cinerariaefolium*	American	.85	1.11	.980
50	*Cinerariaefolium*	All sources	.38	1.21	.640
5	*Roseum*	American, all grades	.25	0.82	.630
10	Unknown, probably *Cinerariaefolium*	Commercial lots	.41	.79	.626

pressed so that such a separation could not be made. The Department of Agriculture samples (numbers 31 to 50 inclusive) had been examined, before powdering, by Mr. George L. Keenan, Microanalyst, Food, Drug and Insecticide Administration. The results showing the percentage of achenes, disk florets, ray florets and receptacles in the twenty powdered samples are Mr. Keenan's and are published by permission. The whole flowers were ground to about 40-mesh, taking care to avoid heating during the grinding.

The pyrethrins, or active principles, were determined by the method previously described;[2] the analyses are reported in Table I and are summarized in Table II.

There was little or no difference in the pyrethrin content of the different grades of Dalmatian flowers. In general, the closed flowers yielded more color and extractive than the open flowers. Some of the samples that had been powdered for several years yielded almost colorless extracts but the pyrethrin content was as high as that of freshly ground new flowers. The pyrethrin content of the Dalmatian flowers ranged from 0.38 to 0.58%. Staudinger and Harder[3] found 0.4 to 0.6% of pyrethrins in the Dalmatian samples they analyzed.

The Japanese flowers contained from 0.58 to 1.21% of pyrethrins and averaged twice the pyrethrin content of the Dalmatian flowers.

It is interesting to note that American grown *Pyrethrum cinerariaefolium* is richer in active principle than Dalmatian and equal to Japanese. American grown *Pyrethrum roseum* averaged higher than Dalmatian *P. cinerariaefolium* and lower than Japanese. Ten commercial samples averaged 0.63%. No connection could be found between the appearance of the flowers and the pyrethrin content.

Summary

Japanese *Pyrethrum cinerariaefolium* has about twice the insecticidal value of Dalmatian flowers. Flowers equal to the Japanese can be grown

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[2] Gnadinger and Corl, THIS JOURNAL, 51, 3054 (1929).

[3] Staudinger and Harder, *Ann Acad Sci. Fennicae*, 29A, 1–14 (1927).

in America. The pyrethrin content of P. *roseum* is about the same as that of P. *cinerariaefolium*.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 226]

ALKALI METAL DERIVATIVES OF PHENYLATED METHANES AND ETHANES

BY CHARLES BUSHNELL WOOSTER[1] AND NEWELL WILSON MITCHELL[2]

RECEIVED JULY 29, 1929 PUBLISHED FEBRUARY 6, 1930

The fact that many of the colored organo-alkali compounds conduct the electric current in ether and in liquid ammonia solution,[3] and behave in other ways as salts, implies that the corresponding hydrides should exhibit an acidic character, albeit an exceedingly weak one. In fact, it has been shown that they may react with the ammono-base, potassium amide, in liquid ammonia solution to form the potassium salts. Thus triphenylmethane forms potassium triphenylmethide[4]

$$(C_6H_5)_3CH + KNH_2 \longrightarrow NH_3 + (C_6H_5)_3CK \qquad (1)$$

and potassium benzhydrolate yields dipotassium benzophenone[5]

$$(C_6H_5)_2CHOK + KNH_2 \longrightarrow (C_6H_5)_2CKOK + NH_3 \qquad (2)$$

This behavior indicates that these hydrides are ionized to a greater degree than the solvent ammonia, for otherwise reaction would be expected to proceed in the opposite direction corresponding to an ammonolysis of the salts. In the case of the alkali alkyls and alkali phenyls[6] such an ammonolysis does occur, demonstrating that the corresponding hydrocarbons are ionized to a less degree than ammonia.[7] Accordingly it is impossible to obtain organo-alkali compounds by the action of potassium amide upon these hydrocarbons.

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[1] National Research Fellow.

[2] A portion of this material was submitted by N. W. Mitchell in a thesis for the degree of Bachelor of Science at the Massachusetts Institute of Technology.

[3] (a) Schlenk and Marcus, *Ber*., 47, 1664–1678 (1914); (b) Kraus and Rosen, THIS JOURNAL, 47, 2739–2740 (1925); (c) Wooster, "Dissertation," Brown University, 1927.

[4] Kraus and Rosen, Ref. 3b, p. 2741.

[5] Wooster, THIS JOURNAL, 50, 1389 (1928).

[6] (a) Kraus and White, *ibid.*, 45, 777 (1923); (b) White, *ibid.*, 45, 779 (1923).

[7] Strictly speaking the ionization of ammonia does not constitute a sharp line of demarcation between hydrocarbons whose salts are completely stable and those whose salts are completely ammonolyzed. Hydrocarbons whose ionization lies either closely above or below that of ammonia would be expected to yield salts whose ammonolysis would reach an equilibrium when appreciable amounts of both the salt and hydrocarbon were present. In all cases considered in this paper, however, the salt was either formed in very large proportions or else in amounts so minute as to escape detection. Thus it is permissible to conclude that the ionization of these hydrocarbons was either considerably above or considerably below that of the solvent.

It is not possible to apply the usual methods to determine the ionization constants of such very weak and sparingly soluble acids, but the facts just reviewed suggest the use of potassium amide in liquid ammonia to differentiate between those hydrides whose ionization is greater and those whose ionization is less than that of this solvent. The results of applying this test to a series of phenylated methanes and ethanes appear in Table I. The action of potassium metal upon the same hydrocarbons in liquid ammonia is also indicated.

TABLE I

THE ACTION OF POTASSIUM AND OF POTASSIUM AMIDE ON PHENYLATED METHANES AND ETHANES

No.	Hydrocarbon formula	Potassium	Potassium amide
1	$C_6H_5CH_3$	No action	No action
2	$(C_6H_5)_2CH_2$	Reacts	Reacts
3	$(C_6H_5)_3CH$	Reacts	Reacts
4	$(C_6H_5)_4C$	No action	No action
5	$C_6H_5CH_2CH_3$	No action	No action
6	$C_6H_5CH_2CH_2C_6H_5$	No action	No action
7	$(C_6H_5)_2CHCH_2C_6H_5$	Reacts	Reacts
8	$(C_6H_5)_3CCH_3$	Reacts slightly	No action
9	$(C_6H_5)_2CHCH(C_6H_5)_2$	Reacts	Reacts
10	$(C_6H_5)_3CCH_2C_6H_5$	Reacts slightly	No action
11	$(C_6H_5)_3CC(C_6H_5)_3$	Adds	...

From these data it is apparent that the ability of potassium amide to replace with potassium a hydrogen atom in hydrocarbons of this class is confined to those compounds (Numbers 2, 3, 7 and 9 in Table I) in which at least two phenyl groups are attached to a single carbon atom. Since no reaction occurs unless a hydrogen atom is also attached to the same carbon atom as are the two or more phenyl groups (see Numbers 4, 8 and 10), it is very likely that it is this hydrogen atom which is replaced. This circumstance may be of use as a principle for deciding the structure of hydrocarbons and organo-alkali compounds of these types.

In certain instances potassium metal is capable of reacting slightly with hydrocarbons on which the amide has no action. This may be due to addition to the carbon–carbon bond between the ethanic carbon atoms, for a similar action of sodium–potassium alloy and of 40% sodium amalgam has been reported by Ziegler and Thielmann and Conant and Garvey.[8] In this connection it is interesting to note that the metal is without action on tetraphenylmethane. This fact favors a negative answer to the question of the partial dissociation of this compound raised by Walden[9] in discussing the molecular weights obtained by Kraus and Kawamura.[10]

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[8] (a) Ziegler and Thielmann, *Ber.*, 5613,1740 (1923); (b) Conant and Garvey, THIS JOURNAL, 49,2599 (1927).

[9] Walden, "Chemie der freien Radikale," Leipzig, 1924, p. 340.

[10] Kraus and Kawamura, THIS JOURNAL, 45,2756 (1923).

The Relative "Electronegativity" of Organic Radicals.—The ionization of toluene is apparently intermediate between that of diphenylmethane and those of benzene and aliphatic hydrocarbons, for although toluene does not react with potassium amide, benzyl bromide and potassium metal yield potassium benzylide which is capable of a transient existence in liquid ammonia as evidenced by its red color and by its reaction with excess benzyl bromide to form dibenzyl. Under similar conditions the alkali phenyls and alkali alkyls are ammonolyzed too rapidly to show such reactions. Thus the ionization of methane (as hydrogen methide) appears to be progressively increased by the substitution of phenyl groups. This is in accordance with Lewis' idea as elaborated in his monograph and with the concepts of Lucas[11] but is the reverse of the series of radicals as arranged in the order of increasing "electronegativity" by Kharasch and Marker.

These authors criticize the conceptions of Lewis in the following terms[12]—"It seems to us, however, more logical that the phenyl radical would in virtue of its electronegativity attract the pair of electrons from the methyl carbon atom, become then negatively charged and repel other electrons from the methyl carbon atom, making the benzyl group much less electronegative than the methyl." In this logic they appear to have overlooked the fact that in attracting the electrons of the methyl carbon atom to a sufficient extent to become negatively charged, as they assume, the phenyl group must leave the former positively charged, with an increased ability to attract electrons, and thus, according to their own definitions more "electronegative."[13]

Moreover, it is difficult to reconcile their conclusions not only with the experimental results which appear in Table I, but also with such a fact as that the substitution of phenyl radicals in ethylene eventually renders the double bond inactive toward bromine but capable of readily adding the alkali metals.[14]

Also, in applying their concepts to the dissociation of free radicals these authors predict that the compound X_3C-CX_3 should be less stable and more highly dissociated than hexaphenylethane whenever the radical X is more "electronegative" than phenyl. This prediction is not supported

[11] (a) Lewis, "Valence and the Structure of Atoms and Molecules," American Chemical Society Monograph, The Chemical Catalog Co., New York, 1923; (b) Lucas, THIS JOURNAL, 48, 1828 (1926).

[12] Kharasch and Marker, *ibid.*, 48, 3138 (1926).

[13] Since this paper was submitted for publication an article by Smyth [ibid., 51, 2386 (1929)] has appeared in which attention is called to the same error in connection with the postulates of Kharasch and Darkis [*Chem. Rev.*, 5, 582 (1928)] regarding the influence of substitution on the polarity of the double bond.

[14] (a) Schlenk, Appendrot, Michael and Thal, ***Ber.***, 47, 473 (1914); (b) Schlenk and Bergmann, ***Ann.***, 463, 2–97 (1928).

by the behavior of dichlorotetraphenylethane,[15] $(C_6H_5)_2CClCCl(C_6H_5)_2$, dichlorotetrabiphenylethane,[16] hexanitroethane[17] and hexachloro-ethane,[18] none of which appear to be dissociated into free radicals. Accordingly, their view that "'. . . . the weight or complexity of the radical is of no significance—it is the electronegativity of the radical attached to the methyl carbon atom that is of paramount importance" is a too narrow one.

Such marked discrepancies cast doubt upon the general applicability of Kharasch and Marker's table of the relative "electronegativity" of organic radicals based upon the reactions between mixed organic mercury compounds and hydrogen chloride. In our opinion it is somewhat premature to draw any general conclusions regarding "electronegativity" from the course of a single class of chemical reactions until due allowance has been made for the influence of such factors as temperature, concentration, nature of solvent and solubility.

Experimental Part

Materials.—The toluene, diphenylmethane, triphenylmethane, ethylbenzene and dibenzyl were obtained from the Eastman Kodak Company and purified by crystallization or distillation. The other hydrocarbons were prepared by processes involving the use of liquid ammonia, as described below.

1,1,1-Triphenylethane was obtained by the action of methyl iodide on potassium triphenylmethide in liquid ammonia. This salt was prepared from potassium and triphenylmethane, the hydrocarbon being used in preference to a halide, in spite of its higher cost, because it could be more readily obtained in a very pure state. The reaction was carried out in the apparatus shown in Fig. 1, consisting of a large Dewar flask C of 1500-cc. capacity, a stirring screw D, operated by a stirring motor, and a rubber stopper fitted with an inlet B and an outlet F for ammonia gas, an opening E for the addition of solid reagents and a dropping funnel A for introducing liquids. The flask was filled two-thirds full of liquid ammonia, the stirrer started and a slow stream of ammonia gas blown through the liquid. The potassium was then introduced and the triphenylmethane **(30 g.)** slowly added in 5-g. portions at about half-hour intervals. Additional pieces of potassium were dropped in from time to time whenever the free metal had entirely reacted, as indicated by a change in color of the solution from opaque blue-black to transparent red. After all of the triphenylmethane had been added and had reacted, methyl iodide was dropped in until the solution became colorless. The equations for the principal reactions are

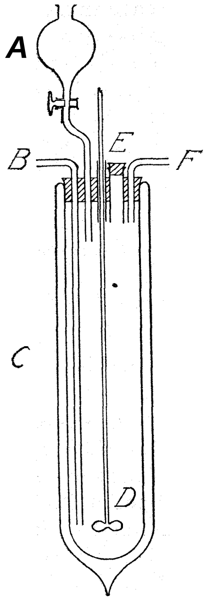

Fig. 1.—Apparatus for organic synthesis in liquid ammonia.

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[15] (a) Schmidlin, *Ber.*, 43, 1153 (1910); (b) Norris, Thomas and Brown, *ibid.*, 43, 2950 (1910).

[16] Schlenk and Kacky, *Ann.*, 394, 211, 215 (1912).

[17] Will, *Ber.*, 47, 963 (1914).

[18] Beilstein, "Handbuch der organischen Chemie," [4] I, 87 (1918); Erstes Erganzungswerk, [4] I, 26 **(1928).**

$$(C_6H_5)_3CH + K \longrightarrow (C_6H_5)_3CK + {}^1/_2H_2 \tag{3}$$

$$(C_6H_5)_3CK + CH_3I \longrightarrow (C_6H_5)_3CCH_3 + KI \tag{4}$$

and this type of synthesis is unique in that the preparation of a hydrocarbon from its next lower homolog is effected in a single process.

Although the liquid ammonia solution became colorless upon the addition of a slight excess of methyl iodide, part of the precipitate formed was light pink in color. This probably consisted of methylammonium triphenylmethide formed as a result of the reactions[19,20]

$$CH_3I + NH_3 \longrightarrow CH_3NH_3I \tag{5}$$

$$CH_3NH_3I + (C_6H_5)_3CK \longrightarrow (C_6H_5)_3CNH_3CH_3 + KI \tag{6}$$

By adding more potassium, continuing the stirring and then again adding a slight excess of methyl iodide, the major portion of this by-product was converted into the desired triphenylethane.

Most of the ammonia was allowed to evaporate. Water was then added to the residue and the aqueous solution filtered. The white solid on the filter paper was washed with water, dissolved in ether, the solution dried, filtered and evaporated and the product recrystallized from alcohol; yield, 85–94% of very pure product melting sharply at 95°.

1,1,1,2-Tetraphenylethane was prepared in a similar manner by the action of benzyl chloride on potassium triphenylmethide and a good yield of the hydrocarbon was obtained. The benzyl chloride was not very rapidly ammonolyzed so it was unnecessary to repeat the treatment with potassium as described in the preceding preparation.

1,1,2-Triphenylethane was obtained by reduction of triphenylethylene with sodium in liquid ammonia and decomposition of the resulting sodium addition product with ammonium chloride,

$$(C_6H_5)_2C{=}CHC_6H_5 + 2Na \longrightarrow (C_6H_5)_2C(Na){-}C(Na)HC_6H_5 \tag{7}$$

$$(C_6H_5)_2C(Na){-}C(Na)HC_6H_5 + 2NH_4Cl \longrightarrow \\ 2NaCl + 2NH_3 + (C_6H_5)_2CH{-}CH_2C_6H_5 \tag{8}$$
[21]

Sym.-tetraphenylethane was obtained from tetraphenylethylene by the method just described under 1,1,2-triphenylethane.

Tetraphenylmethane was prepared by the method of Kraus and Kawamura.[22]

Special Method of Purification.—Although the hydrocarbons prepared from triphenylmethane possessed sharp melting points and other attributes of a high degree of purity, they were always contaminated with exceedingly slight traces of triphenylmethane, just sufficient to interfere with the observation of their behavior with potassium and potassium amide. In the case of those hydrocarbons which react but slightly or not at all with potassium amide, the impurity may be removed by a thorough treatment of the product with this amide, which converts the triphenylmethane into its potassium salt. This salt may then be oxidized with a stream of dry air, forming triphenylmethyl peroxide, which is insoluble in ether and may thus be separated from the soluble hydrocarbons. (Tetraphenylmethane, which is itself almost insoluble in ether, may be freed from triphenylmethane by repeated crystallization from this solvent.)

The study of the hydrocarbons formed by attaching aliphatic radicals to the tri-

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[19] Compare White, Morrison and Anderson, THIS JOURNAL, 46, 963 (1924).

[20] In a trial experiment this pink precipitate was found to decompose with loss of color upon warming to room temperature. The products are probably triphenylmethane and methylamine. This behavior is analogous to that of ammonium triphenylmethide (Ref. 10, p. 2758).

[21] Evidence that the disodium derivative is partly ammonolyzed to $(C_6H_5)_2C(Na)$-$CH_2C_6H_5$ will be presented in a forthcoming article.

[22] Kraus and Kawamura, Ref. 10, p. 2760.

phenylmethyl group which was made by Gomberg and Cone[23] was apparently rendered more difficult by the trouble of separating the product desired from the quantities of triphenylmethane also formed. The process just described promises to remove this difficulty satisfactorily.

The Action of Potassium and of Potassium Amide on the Hydrocarbons.—These reactions were carried out in a small reaction tube connected to an apparatus similar to that previously described.[24] Potassium metal was converted to the amide in liquid ammonia solution by the catalytic action of a piece of rusty iron. The hydrocarbon was then added to this pale yellow solution. In all cases but one[25] where reaction was observed, an intense red or orange-yellow coloration resulted in a very short time and most of the hydrocarbon was seen to dissolve In all cases where no action was reported, no change in color was observed after the mixture had been stirred for at least thirty minutes and the hydrocarbon was recovered unchanged at the end of the experiment. In studying the action of the metal itself, a mixture of the hydrocarbon and the solution of potassium was stirred for thirty minutes, the iron oxide catalyst then added and the color observed after all of the free metal had been converted into the amide.

The Action of Alkali Metals on Benzyl Bromide.—In 1923, Kraus and White[26] observed a reaction between sodium and benzyl chloride in liquid ammonia, but did not characterize the products. This experiment was repeated with benzyl bromide, adding one equivalent to a solution of two equivalents of sodium in liquid ammonia. Reaction took place rapidly, but the solution remained blue in color and, therefore, contained free sodium. More of the bromide was added until the blue color was discharged and replaced by a deep, rich, red color which gradually faded until the solution became entirely colorless. A white precipitate was then visible. The solid product obtained by extraction of the residue with ether could not be readily purified by crystallization, but upon subjecting it to sublimation from an oil-bath, crystals were collected which melted at 52° and proved to be dibenzyl. A similar reaction was observed with potassium. The red color of the liquid ammonia solution indicated the presence of sodium benzylide, which reacted with excess benzyl bromide to form dibenzyl.

Thus far the action of sodium on alkyl or aryl monohalides in liquid ammonia has always followed one of two distinct courses. When the hydrocarbon residue has been unable to form a sodium salt which is stable in ammonia, the product has consisted of the hydrocarbon and amines corresponding to the halide used. This has been the case when alkyl or phenyl[27] halides were employed[6] and is expressed in the equation

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[23] Gomberg and Cone, *Ber.*, **39,** 2957 (1906).

[24] Wooster, THIS JOURNAL, 51, 1856 (1929).

[25] The reaction between *sym.*-tetraphenylethane and potassium amide in liquid ammonia proceeds slowly. This is doubtless due to the exceedingly low solubility of the hydrocarbon, since the addition of toluene promotes the reaction. The best result was obtained when a toluene solution of the hydrocarbon was added to the liquid ammonia solution of the amide. The stability of toluene and ethylbenzene toward potassium amide cannot be ascribed to solubility influences since these substances are more soluble in ammonia than those hydrocarbons which react readily with the amide [Franklin and Kraus, *Am Chem.* J.,20,820 (1898)]. In all other instances where no action is reported the experiments were repeated using a toluene solution of each hydrocarbon but no difference in the results was observed.

[26] Kraus and White, Ref. 6a, p. 773.

[27] In this connection it must be noted that *traces* of biphenyl have been observed in a few instances.

$$2RCl + NH_3 + 2Na \longrightarrow RH + RNH_2 + 2NaCl \qquad (9)$$

although in practice, secondary and tertiary amines may also be formed.

On the other hand, when the hydrocarbon residue is capable of forming a sodium salt which is stable in ammonia, this salt results when the proportions of the reacting materials are correct.

$$RCl + 2Na \longrightarrow NaCl + RNa \qquad (10)$$

By further addition of the same or a different halide a synthesis of the Wurtz–Fittig type may be accomplished.

$$RNa + R'Cl \longrightarrow RR' + NaCl \qquad (11)$$

The reaction of benzyl bromide, therefore, presents an example of a new and intermediate case for although the sodium salt is unstable in ammonia, the reaction proceeds in such a manner that a synthesis of the Wurtz–Fittig type is possible. A further study of this reaction may yield considerable information regarding the mechanism of reduction by the alkali metals in liquid ammonia.

Summary

1. The acid character of hydrogen atoms in the side chains of aromatic hydrocarbons has been investigated. A table of the results has been prepared which illustrates the influence of the number and positions of the phenyl groups in the compound.

2. The influence of phenyl substitution upon the stability of certain organo-alkali compounds in ammonia is contrasted with the conclusions of Kharasch and Marker regarding the relative "electronegativity" of organic radicals.

3. Synthetic methods for the preparation of certain hydrocarbons in liquid ammonia solution are described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO METHYL TIN DERIVATIVES. V. ACTION OF SODIUM TRIMETHYL TIN ON METHYLENE CHLORIDE

BY CHARLES A. KRAUS AND ARTHUR M. NEAL

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A. Di-Trimethylstannylmethane

Kraus and Greer[1] studied the action of methylene chloride on disodium dimethyl tin and found that the organic group combines with the dimethyl tin group to form a compound that has a marked tendency to polymerize. Kraus and Sessions[2] treated sodium trimethyl tin with symmetrical ethylene chloride. The products of reaction proved to be sodium chloride, trimethyl tin and ethylene. It seemed worth while to study the corresponding reaction between sodium trimethyl tin and methylene chloride in liquid ammonia. This reaction might be expected to proceed according to the equation

$$2(CH_3)_3SnNa + CH_2Cl_2 = [(CH_3)_3Sn]_2CH_2 + 2NaCl$$

Experiment showed that reaction takes place quantitatively, as was anticipated, but in attempting to characterize the compound by its reaction with sodium in liquid ammonia, certain unexpected reactions occurred. These were followed up further and are described in the next section.

Preparation.—A quantity of trimethyl tin bromide was dropped slowly into several hundred cubic centimeters of liquid ammonia contained in a Dewar flask. Sodium was then added until the compound was completely reduced to a sodium trimethyl tin. The end-point of the reaction is indicated by the appearance of a permanent blue color due to free sodium.

On now adding methylene chloride to the solution of sodium trimethyl tin, immediate reaction occurred with the formation of a liquid precipitate. When the reaction was completed, the supernatant liquid was colorless. The ammonia was allowed to evaporate and the oil was washed several times with distilled water, from which it was then separated. It was dried by filtering through anhydrous sodium sulfate in an atmosphere of nitrogen. Samples of the oil were introduced into weighed tubes and sealed under an atmosphere of nitrogen.

Analyses **and** Molecular Weight.—The compound was analyzed for tin by the Carius method. Subs. 0.3865, 0.6605, 0.6941: SnO_2, 0.3451, 0.5841, 0.6120. Calcd. for $[(CH_3)_3Sn]_2CH_2$: Sn, 69.50. Found: Sn, 70.33, 69.66, 69.45. The molecular weight was determined in benzene by the freezing-point method: solvent, 17.66, 20.85; solute, 0.7387, 0.9903; At, 0.590, 0.682"; mol. wt. found, 354.6, 348.2. Calcd. for $[(CH_3)_3Sn]_2CH_2$: 341.6.

Properties.—Di-trimethylstannylmethane is a colorless liquid which is quite fluid at liquid ammonia temperatures. It boils at 199–201° under normal pressure.

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[1] Kraus and Greer, THIS JOURNAL, 47, 2568 (1925).

[2] Kraus and Sessions, *ibid.*, 47, 2361 (192.5).

The compound is readily iodized in benzene or chloroform solution. In two experiments 2.1 and 1.99 moles of iodine were required per mole of the compound. Reaction thus takes place according to the equation

$$[(CH_3)_3Sn]_2CH_2 + 2I_2 = 2(CH_3)_3SnI + CH_2I_2$$

After iodination in chloroform, the trimethyl tin iodide was precipitated by means of ammonia. Analysis of the product showed that it consisted of the ammonia complex $(CH_3)_3SnI{\cdot}NH_3$. From the filtrate there was obtained a product melting unsharply at 2°. This was evidently impure methylene iodide, which melts at 5.7°.

B. Action of Sodium on Di-Trimethylstannylmethane and Allied Reactions

In order to establish further the constitution of the compound whose preparation has been described in the preceding section, it was reduced with sodium in liquid ammonia and the resulting products were studied. In general, when a metallo-organic compound of the type R_4M is reduced with sodium in liquid ammonia, the following reaction occurs

$$R_4M + 2Na + NH_3 = R_3MNa + NaNH_2 + RH \qquad \text{(I)}$$

Reaction might also be expected to occur according to the equation

$$2R_4M + 2Na = 2R_3MNa + R_2 \qquad \text{(II)}$$

However, this latter reaction occurs infrequently, except when one of the substituents R is hydrogen.

Preliminary Experiments.—A weighed quantity of di-trimethylstannylmethane was treated with sodium in liquid ammonia. The metal was introduced, a little at a time, until the reduction was completed and the amount of sodium added was determined by weighing back. Gas evolved in the course of the reduction was collected over water and its volume and density were determined. Ammonium bromide was then added to the reaction mixture and the gas evolved in this reaction was collected over water and its volume and density were determined.

It was anticipated that, in the initial process of reduction, reaction would occur according to the equation

$$[(CH_3)_3Sn]_2CH_2 + 4Na + 2NH_3 = 2(CH_3)_3SnNa + 2NaNH_2 + \mathrm{CH_I} \qquad \text{(III)}$$

Since sodium amide is difficultly soluble in liquid ammonia, it was expected that it would be precipitated. A precipitate of sodium amide was, in fact, formed as the reaction proceeded. On adding ammonium bromide to the products of this reaction, it was anticipated that the sodium amide would be neutralized by the ammonium bromide, according to the equation

$$NaNH_2 + NH_4Br = NaBr + 2NH_3 \qquad \text{(IIIA)}$$

while the sodium trimethyl tin should be converted to the stannane, according to the equation

$$(CH_3)_3SnNa + NH_4Br = NaBr + (CH_3)_3SnH + NH_3$$

Two reactions were carried out in which, respectively, 6.4 and 6.8 m. moles of di-trimethylstannylmethane were treated with 21.6 and 23.2 m. atoms of sodium and 94.2

and 101.9 (4.2 and 4.6 m. moles) cc. of gas were evolved. The density of the gas indicated a mean molecular weight of 19.6 and 18.8, respectively. In the two experiments, 3.6 and 3.4 m. atoms of sodium were required per mole of compound in order to complete the reduction. According to Equation III, 4 atoms of sodium are required per mole of compound. The discrepancy is probably due to loss of the original material, which is appreciably volatilized in the course of the process of reduction. The molecular weight of the gas indicated that it was probably methane.

On adding ammonium bromide to the product of the above reductions, the solid (sodium amide) dissolved and a gas was evolved. In the two experiments, respectively, 12.7 and 14.1 m. moles of ammonium bromide were required to complete the initial stage of the reaction. This is approximately 2 moles of ammonium bromide per mole of the original compound. The density of the evolved gas in the two experiments corresponded to a molecular weight of 10.3 and 14.0, indicating that it consisted of hydrogen admixed with an impurity. On disappearance of the solid precipitate, a clear yellow solution remained. It was inferred that this color was due to sodium trimethyl tin. On further addition of ammonium bromide, no gas was evolved and a liquid was precipitated while the yellow color disappeared. The liquid proved to be trimethylstannane.

The appearance of hydrogen on addition of ammonium bromide to the products of reduction was unexpected. If ammonium bromide reacted with sodium amide according to Equation IIIA, no hydrogen would be produced, while any ammonium bromide reacting with sodium trimethyl tin is known to form trimethylstannane. The reaction between sodium amide and trimethylstannane has not been previously studied. It is known, however, that the alkali metal amides react readily with triphenylmethane according to the equation

$$(C_6H_5)_3CH + NaNH_2 = (C_6H_5)_3CNa + NH_3$$

Since sodium trimethyl tin is highly soluble and sodium amide is only sparingly soluble in liquid ammonia, it is to be expected that, on adding ammonium bromide to a mixture of the two in liquid ammonia, trimethylstannane would first be formed and that this compound would then react with the sodium amide present. Accordingly, it was found necessary to study the action of sodium amide on trimethylstannane.

The high values found for the molecular weights of the gases produced in the reactions described above indicated that volatile tin compounds were carried over with the escaping gases. Kraus and Sessions[2] found this to be the case in the reduction of tetramethyl tin. Accordingly, in subsequent experiments the evolved gases were passed through a strong solution of sodium in liquid ammonia, prior to collecting them over water. In order to establish the nature of the reduction process in the case of di-trimethylstannylmethane, the reaction between trimethylstannane and sodium amide was first studied. To establish the nature of this reaction fully, it was found necessary to study also the reaction between sodium amide and trimethyl tin. Finally, the reduction of di-trimethylstannylmethane was repeated and the products of reaction were identified.

Action of Sodium Amide on Tri-methylstannane.—A known weight of trimethyl tin bromide was introduced into a reaction tube and dissolved in liquid ammonia. The bromide was reduced to sodium trimethyl tin by means of sodium and this, in turn, was converted to trimethylstannane by addition of an equivalent quantity of ammonium bromide. To this preparation sodium amide was added until reaction was complete. Gas was evolved throughout this reaction; it was collected over water and its density determined. In a second experiment the evolved gas was passed through a solution of sodium in liquid ammonia prior to collecting over water.

In two experiments, respectively, 15.4 and 15.4 m. moles of trimethylstannane were treated with 20.8 and 14.3 m. moles of sodium amide with the evolution of 4.35 and 2.06 m. moles of gas. The density of the gas in the first reaction, collected directly over water, corresponded to a molecular weight of 28.1, while that of the second reaction washed through a sodium solution was 4.80. Because of the low solubility of sodium amide, an excess of this substance was added in both experiments in order to complete the reaction, and the proportion of this material to the stannane is without significance. However, in the first experiment, 0.28 mole of gas was evolved per mole of stannane, and in the second only 0.13 mole. Seemingly, several reactions occur in varying proportions, depending upon the conditions of the experiment. That the evolved gas was hydrogen is clearly shown by the low value of the molecular weight in the second experiment.

The reactions may be formulated as follows

$$(CH_3)_3SnH + NaNH_2 = (CH_3)_3SnNa + NH_3 \qquad \text{(IV)}$$

$$2(CH_3)_3SnH + NaNH_2 = (CH_3)_3SnNa + (CH_3)_3SnNH_2 + H_2 \qquad \text{(V)}$$

The proportion in which the two reactions take place probably depends upon the concentration and state of subdivision of the reacting materials.

Sodium amide is only slightly soluble in liquid ammonia, and in order to obtain a quantity of this material in a finely divided condition, the preceding experiment was repeated with some modification. Tetramethyl tin was treated with an equivalent quantity of metallic sodium. According to Kraus and Sessions,[2] this reaction leads to the formation of a solution of sodium trimethyl stannide and a finely divided precipitate of sodium amide in equivalent amount. Ammonium bromide was added to the resulting solution. Because of the relatively low solubility of sodium amide, and perhaps for other reasons, the ammonium bromide initially reacts with sodium trimethyl stannide to form trimethylstannane, which, in turn, reacts with sodium amide. The gas evolved, on addition of ammonium bromide, was passed through a concentrated solution of sodium in liquid ammonia prior to collecting it over water.

In this reaction 11.9 m. moles of tetramethyl tin were treated with 23.8 m. atoms of sodium, which resulted in the production of a solution containing 11.9 m. moles of sodium trimethyl stannide and 11.9 m. moles of finely divided sodium amide. This was treated with 13.3 m. moles of ammonium bromide; 83.0 cc. of gas was evolved, having a mean molecular weight of 5.01. The volume of gas corresponded to 3.7 m. moles, or 7.4 m. atoms of hydrogen. Therefore, 62% of the stannane formed in the course of the reaction was converted to sodium trimethyl stannide and trimethyl tin amine, according to Equation V.

The isolation of trimethyl tin amine involves many difficulties and its presence was accordingly shown by certain characteristic reactions. When sufficient ammonium bromide had been added to the initial reduction product to react with all the sodium amide, the solution, which was now transparent and of a pale yellow color, was treated with sodium. No gas was evolved but a finely divided precipitate was formed having the characteristics of sodium amide. Reaction occurred according to the equation

$$(CH_3)_3SnNH_2 + 2Na = (CH_3)_3SnNa + NaNH_2 \qquad \text{(VI)}$$

In order to show that the precipitate formed in this reaction was sodium amide, the mixture was treated with ammonium bromide. This was thus a repetition of Reaction V. On addition of ammonium bromide, a gas was evolved, and this evolution of gas continued until the precipitate had disappeared. This behavior is characteristic of a mixture of sodium trimethyl stannide and sodium amide. Further addition of ammonium bromide caused precipitation of trimethyl stannane.

Basing our calculation on the amount of hydrogen evolved in the preceding reaction, there were present in the solution 3.7 m. moles of trimethyl tin amine. To this solution were added 6.8 m. atoms of sodium and, on addition of excess ammonium bromide, there was evolved 31.8 cc. of gas, or 1.42 m. moles, having a mean molecular weight of 4.6. The amount of gas evolved corresponds to a reaction in which 75% of the product, formed according to Equation VI, reacted according to Equation V when ammonium bromide was added.

On adding ammonium bromide to a solution of sodium trimethyl stannide, in the presence of sodium amide, reaction takes place, initially according to the equation

$$(CH_3)_3SnNa + NH_4Br = (CH_3)_3SnH + NaBr + NH_3 \qquad \text{(VII)}$$

The trimethylstannane resulting from this reaction then reacts to the extent of about 70% according to Equation V, and 30% according to Equation IV.

Action of Sodium Amide on Trimethyl Tin.—In order to obtain some further data relative to trimethyl tin amine, the reaction between trimethyl tin and sodium amide was studied. Owing to the low solubility of both constituents in liquid ammonia, reaction takes place slowly according to the equation

$$[(CH_3)_3Sn]_2 + NaNH_2 = (CH_3)_3SnNa + (CH_3)_3SnNH_2 \qquad \text{(VIII)}$$

A slight excess of sodium amide was added in order to ensure completion of the reaction. The resulting solution exhibited the characteristic yellow color of sodium trimethyl stannide. Since trimethyl tin amine is volatile, its presence was shown by evaporating the ammonia solution into water, acidifying the aqueous solution with sulfuric and nitric acids and evaporating to dryness. As the result of this procedure, a small quantity of stannic oxide was obtained, indicating that a volatile tin compound was carried over with the ammonia vapors. In another experiment the ammonia was recondensed and sodium was added to the condensate. Immediate reaction took place, the solution acquired a yellow color, characteristic of sodium trimethyl stannide, and a finely crystalline precipitate was formed which resembled sodium amide. These observations would seem to demonstrate the presence of trimethyl tin amine as one of the products of reaction between sodium amide and trimethyl tin.

Final Reduction of Di-trimethylstannylmethane with Sodium.—With a knowledge of the action of sodium amide on trimethylstannane, it was possible to repeat the reduction of di-trimethylstannylmethane and to interpret the results with a reasonable degree of certainty. Sodium was added to a weighed quantity of the tin derivative in liquid ammonia until the end-point was reached, which was indicated by the appearance of a permanent blue color due to free metal. The data relating to this experiment are as follows: $[(CH_3)_3Sn]_2CH_2$, 1.4881 g. (4.35 m. moles); Na, 0.3505 g. (15.24 m. atoms); evolved gas, 66.95 cc. (2.99 m. moles); molecular weight of gas 15.99. On adding ammonium bromide, there was evolved a gas whose mean molecular weight was found to be 3.8.

As follows from these data, 3.5 atoms of sodium was used per mole of compound in the process of reduction. According to Equation III, 4 atoms are required. The discrepancy is doubtless due to unavoidable loss of material as a result of the volatility of trimethylstannane. The gas evolved in the course of reduction had a molecular weight corresponding closely to that of methane. The volume of methane obtained was somewhat low owing to the loss of some of the material. The gas evolved, on addition of ammonium bromide, was unquestionably hydrogen. The somewhat high value of its molecular weight was doubtless due to the presence of a small quantity of volatile tin compounds as impurities. It is almost impossible to avoid the presence of some of these compounds in the collected gases. Indeed, it was necessary to clean carefully all of the connecting tubes of the apparatus prior to carrying out an experiment; otherwise, much higher values were obtained.

The reaction evidently takes place according to Equation III. It probably occurs in two stages, as follows

$$[(CH_3)_3Sn]_2CH_2 + 2Na + NH_3 = (CH_3)_3SnNa + (CH_3)_3SnCH_3 + NaNH_2$$
$$(CH_3)_3SnCH_3 + Na + NH_3 = (CH_3)_3SnNa + CH_4 + NaNH_2$$

Summary

Di-trimethylstannylmethane, $[(CH_3)_3Sn]_2CH_2$, has been prepared and some of its properties investigated. It boils at 199–201° and has a normal molecular weight in benzene.

It has been shown that when sodium amide reacts with trimethylstannane in liquid ammonia, two reactions occur simultaneously. In one of these sodium trimethyl stannide and ammonia are formed, while in the other sodium trimethyl stannide, trimethylstannylamine and hydrogen are produced. The proportion in which these two reactions occur depends upon conditions, Sodium amide reacts with trimethyl tin to form sodium trimethyl stannide and trimethylstannylamine.

When ammonium bromide is added to a solution of sodium trimethyl stannide and sodium amide, hydrogen is evolved. For the most part, the ammonium bromide reacts with the stannide to form trimethylstannane, which in turn reacts with sodium amide, a portion to form sodium trimethyl stannide directly and another portion to form sodium trimethyl stannide, sodium trimethylstannylamine and sodium amide.

When di-trimethylstannylmethane is reduced with sodium in liquid ammonia, sodium trimethyl stannide is produced and methane is evolved.

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[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORIES OF THE UNIVERSITY OF UPSALA AND THE NEW YORK AGRICULTURAL EXPERIMENT STATION]

THE MOLECULAR WEIGHT OF CASEIN. II

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In a former publication[2] the writers have described their experiments dealing with the molecular weight of casein prepared by the method of Hammarsten and that portion of Hammarsten casein which is soluble in hot acidified 70% alcohol. The first mentioned material was found by the ultracentrifuge to be a mixture of proteins of different molecular weights, while the latter was found probably to be a distinct chemical entity having a molecular weight of 375,000.

It was pointed out in the first paper that the casein that has furnished the starting point for experimental studies in late years has been usually prepared either by the precipitation method of Hammarsten[3] or by the method of Van Slyke and Baker.[4] In the former method the precipitation was effected by the slow addition of dilute acetic acid to milk, while in the latter method normal lactic acid or a mixture of normal acetic and hydrochloric acids was recommended. The latter workers also introduced rapid agitation as a means of distributing the added acid throughout the milk.

One of the principal differences between the two methods seems to lie in the time interval during which the milk is held in a state of partial coagulation. The other principal difference is that Hammarsten redissolves the precipitated casein in dilute alkali and reprecipitates with acid several times, with the hope of removing other substances carried down during the initial precipitation; while on the other hand, Van Slyke and Baker make no attempt to remove organic impurities by reprecipitation

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[1] Fellow of the International Education Board.

[2] Svedberg, Carpenter and Carpenter, THIS JOURNAL, 52, 241 (1930).

[3] E. Abderhalden, "Handbuch der biochemischen Arbeitsmethoden," Berlin und Wien, 1910, Vol. II, p. 384.

[4] Van Slyke and Baker, *J. Biol. Chem.*, 35, 127 (1918).

of the casein. The latter workers seem to be more concerned with reducing the ash content than in separating one protein from another in pure form. These authors claim to produce a pure protein by a single precipitation from the very complex mixture of substances that are known to occur in milk. The work described in this paper will deal with casein prepared from cow's milk by the method described by Van Slyke and Baker.

Experimental Part

Preparation of Material.—We have carried out the precipitation process as described by Van Slyke and Baker using the acetic–hydrochloric acid mixture as precipitant, but have not attempted as yet to dry the material by their method, preferring for the present to make progress with material which had not been subjected to any drying process.

Freshly drawn milk was handled as described in our first paper[2] up to the point where it had passed through the separator. It was then, without diluting, precipitated by Van Slyke and Baker's method. After separating the precipitated casein centrifugally from the solution, the casein was beaten up with water, first to a thin paste by means of an electrically driven stirrer, and then more water was added and the stirring continued until the casein was well distributed throughout the whole of the wash water. After allowing to stand for an hour or so, the casein was separated centrifugally from the wash water. The washing was repeated in this manner five or six times, the washed casein finally being stored under water with toluene at 5°. Several such preparations were made at various times and used during the course of the work.

The same technique of preparing the casein solutions was used as was given in the first paper, namely, dissolving two grams of casein (dry basis) in 25 cc. of $M/15$ mixed phosphate buffer solution at PH 6.8 and diluting this to 100 cc., thereby producing a $M/60$ buffer salt concentration. The solution was prepared in the cold, slowly passed through the milk separator driven at a high speed and stored at 5° with toluene as preservative. The protein content of this solution was determined by evaporating *a* sample to dryness at 105° and correcting the weight of residue for the buffer salts present. Dilutions were made from the stock solution as required for the centrifuging work. No material changes were made in the centrifuging set-up or technique, which has already been described.

Determination of Molecular Weight.—In the experiments immediately following, the sedimentation velocity method was applied. Owing, however, to the fact that no constant diffusion value was obtainable from Van Slyke and Baker's casein, on account of its being a mixture, we are unable to use the usual molecular weight equation $M = RTS/D(1 - V\rho)$, where R is the gas constant, T the absolute temperature, S the specific sedimentation velocity or $1/\omega^2x\cdot dx/dt$, D the diffusion constant, V the partial specific volume of the protein, ρ the density of the solvent, x the distance from the axis of rotation, ω the angular velocity and t the time. We must, therefore, rely upon sedimentation velocity measurements entirely for a solution of the problem.

According to Stokes' Law for a spherical particle of radius r_1

$$^4/_3\pi r_1^3(\rho_1 - \rho_2) = 6\pi h r_1 s_1 \qquad (1)$$

and for any other spherical particle of radius r_2

$$^4/_3\pi r_2^3\ (\text{PI} - \rho_2) = 6\pi h r_2 s_2 \tag{2}$$

where $(\rho_1 - \rho_2)$ represents the difference in density between the particle and solvent and s_1 and s_2 represent the specific sedimentation velocities of the two particles of radius r_1 and r_2, respectively.

If we assume that the two particles have the same partial specific volume, then dividing (1) by (2) we obtain

$$\frac{r_1}{r_2} = \left(\frac{s_1}{s_2}\right)^{1/2} \tag{3}$$

However, where M_1 and M_2 represent the molecular weight of the respective species

$$\frac{M_1}{M_2} = \left(\frac{r_1}{r_2}\right)^3 \tag{4}$$

from which

$$\frac{M_1}{M_2} = \left(\frac{S_1}{S_2}\right)^{3/2} \tag{5}$$

In Tables I and II are given data on specific sedimentation velocity and diffusion, respectively, for a typical run at 1.0% protein concentration.

TABLE I

VAN SLYKE AND BAKER CASEIN. SEDIMENTATION VELOCITY RUN

Initial protein concentration, *1.00%;* solvent, $M/60$ mixed phosphate buffer at P_H *6 8;* speed, *42,000* r.p m. (ω = *1399 8* π); interval between exposures, *20* min.; *T*, *298.4";* illumination, mercury lamp; light filters, Cl_2 and Br_2; Imperial Process photographic plates; exposure time, *45* sec.; metol–hydroquinone developer; development time, *2* min.

Sedimentation curves *used* in calcn [a]	Δx, cm.	x, mean, cm.	$S_{20°}$, cm. $\times 10^{13}$
3 4	*0.070*	*4.775*	*5.60*
4–5	.078	*4.849*	*6.15*
5–6	.076	*4.926*	*5.89*
6–7	.077	*5.002*	**5.88**
7–8	.075	*5.078*	*5.64*
8–9	.076	*5.154*	*5.63*
9-10	.078	*5 228*	*5.70*
		Mean	*5.78*

[a] Sedimentation curves bear the same number in Fig. *2* as in these data.

In Fig. 1 is shown a photographic record of a sedimentation series at 1.0% initial concentration. The top row of exposures represents the progress of the sedimentation, beginning at the left side, with a centrifuge speed of 42,000 r.p.m. The lower row of exposures represents the concentration scale by regular increments from pure buffer solution on the left to the initial protein concentration on the right. In Fig. 2 are shown the sedimentation curves, showing the distribution within the cell during the progress of the sedimenting experiment. To arrive at an approximation of the molecular weight of the main bulk of the protein in this material

TABLE II

VAN SLYKE AND BAKER CASEIN. DIFFUSION MEASUREMENTS

Initial protein concentration, 1.00%; same experimental details as given in Table I

Reading	Diffusion time, sec.	Mean[b] Z, cm	"Apparent" $D_{20°}$, cm.^{2}/sec. $\times 10^7$
3	1500	0.0170	1.84
4	2700	.0295	3.08
5	3900	.0395	3.83
6	5100	.0465	4.06
7	6300	.0565	4.85
8	7500	.0690	6.07
9	8700	.0820	7.40
10	9900	.0950	8.72

[a] Reading numbers refer to corresponding sedimentation curves in Fig. 2.

[b] "Mean Z" represents the mean of the distances from C = 25% to C = 50% and from C = 50% to C = 75% (see THIS JOURNAL, 49, 2922 (1927)).

we have considered the break in the curves of this series to occur at the point of intersection with the line AB.

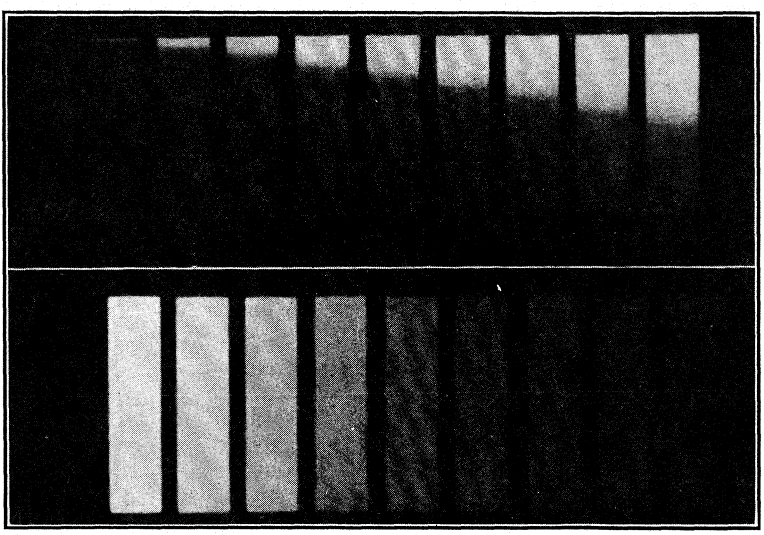

Fig. 1.

The shape of the sedimentation curves in Fig. 2 indicates that casein prepared by the method of Van Slyke and Baker is little or no improvement over the Hammarsten method. The material is definitely not one single protein substance but contains several kinds of molecules of different weights. The sedimentation values as shown in Table I are fairly constant, but the "apparent" diffusion values given in Table II show that as the experiment proceeds these values increase and are not constants such as we would have were we dealing with a homogeneous substance. The increase in the "apparent" diffusion is attributed to a spreading out of the boundary due to the effect of the centrifugal force on particles of different size. On the assumption that we are dealing with a spherical particle, we have calculated the theoretical distribution at the boundary after two hours of centrifuging of a monomolecular system having the specific sedimentation velocity we have found experimentally, and represented it as curve C in Fig. 2. As the above assumption involves the condition of minimum frictional resistance of the particle and consequently the maximum possible diffusion, we must conclude that there are protein molecules of at least three different sizes in Van Slyke and Baker's casein, one being larger and one considerably smaller than the main bulk of the material.

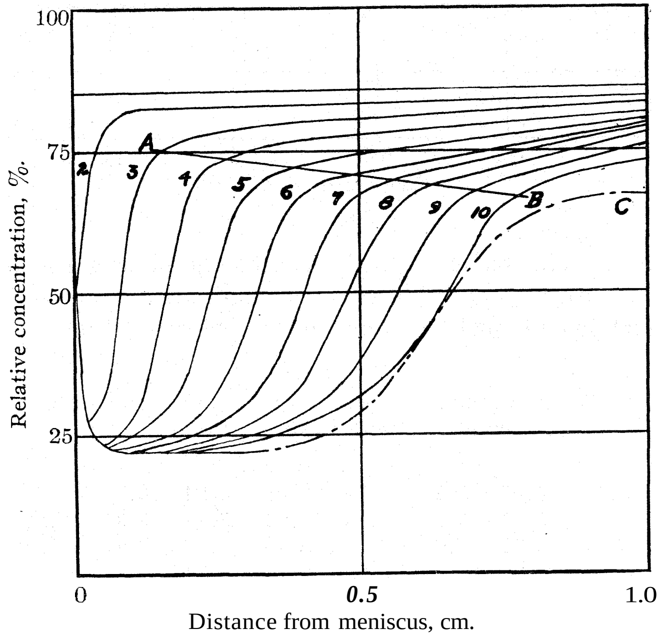

Fig. 2.

In Table III is given a summary of a large number of sedimentation velocity measurements on two different samples of Van Slyke and Baker casein at various protein concentrations. In Fig. 3 these data are shown graphically. It is to be noted that the influence of protein concentration on the sedimentation velocity is practically constant down to a concentration of about 0.50%, below which value the sedimentation velocity drops off rather rapidly. As the region between 0.50 and 2.00% seems to indicate a reasonably constant condition of the protein molecules, we will confine our attention largely to this region. Within this concentration range the main component of this protein mixture behaves very differently from the acidalcohol soluble casein which we described in a former publication.[2] The latter protein was more stable in dilute solutions (below 0.45%), while this protein appears to be more stable at concentrations above 0.50%. The buffer salt, the concentration and PH have been exactly alike with respect to both proteins, and identical procedures were used in dissolving the moist proteins in this buffer solution.

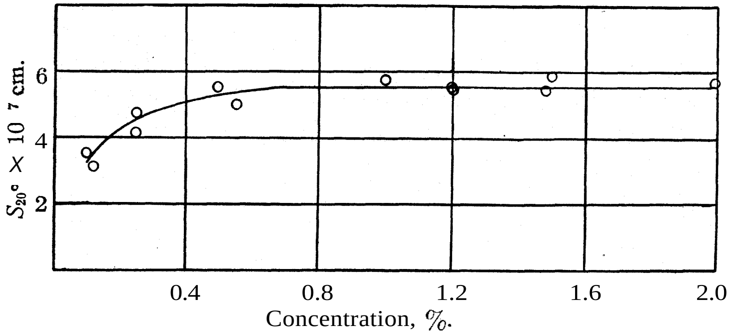

Fig. 3.

TABLE III

VAN SLYKE AND BAKER CASEIN. SUMMARY OF SEDIMENTATION VELOCITY MEASUREMENTS AT VARIOUS CONCENTRATIONS

Init. concn., %				$S_{20} \times 10^{13}$ cm./sec.					Mean
2.00	5.18	5.05	5.43	5.79	6.01	6.24	6.05	6.21	5.74
1.50		5.85	5.72	6.10	5.92	5.88	5.92	0.20	5.94
1.48		5.32	5.63	5.46	5.39	5.17	5.71		5.47
1.20				5.39	5.13	5.73			5.42
1.20			5.44	4.96	5.60	5.88	5.86		5.55
1.00		5.60	6.15	5.89	5.88	5.64	5.63	5.70	5.78
0.55			5.12	4.81	4.83	5.07	5.02		4.97
.50		5.60	5.13	5.06	5.38	5.30	5.46		5.32
.25			4.63	4.79	4.94	4.88			4.81
.25				4.02	4.40	3.99			4.10
.12			3.06	3.18	3.07	2.95			3.09
.10			3.69	3.24	3.24	3.69			3.47

The two samples of Van Slyke and Baker casein shown in Fig. 3 show differences between themselves, one apparently being a purer specimen than the other. Some preliminary results which we have obtained by fractionating Van Slyke and Baker casein with potassium oxalate indicate that the purer of the two samples is the one having the smaller sedimentation velocity. For the purposes of the calculations of this paper, however, we have taken a mean of the 47 specific sedimentation velocity values recorded in Table III at concentrations of 0.50% and above, where the molecule is comparatively stable. This mean value is $S_{20^\circ} = 5.56 \times 10^{-13}$ and is probably somewhat greater than the true value representing the pure protein, on account of the fact that it represents an average obtained with specimens both of which contained a protein of rather high molecular weight as impurity.

It has been shown that for spherical particles having the same partial specific volume $M_1/M_2 = (S_1/S_2)^{3/2}$, where M_1 and S_1 represent the molecular weight and specific sedimentation velocity, respectively, of one chemical species and M_2 and S_2 the corresponding values of some other species. The egg albumin molecule has been deduced to be spherical in shape, to have a molecular weight of 34,500 and S_{20° equal to 3.32×10^{-13} and a partial specific volume of 0.748, almost identical with the value of 0.750 for casein.[5] Using this as a reference substance, from the above relationship we calculate that the molecular weight of Van Slyke and Baker casein cannot be less than 75,000.

Assuming a spherical particle and applying Stokes' Law $r = \sqrt{\frac{9}{2}\frac{hS}{(\rho_1 - \rho_2)}}$, where r equals the particle radius, h the viscosity of the solvent, S the specific sedimentation velocity and $(\rho_1 - \rho_2)$ the difference in density between particle and solvent, we calculate the molecular radius to be 2.75×10^{-7} cm. The majority of the proteins which have been examined to date, however, do not seem to have spherical shaped molecules, but are of some different shape which operates to increase the frictional resistance and the effective radius of the particle. We have calculated this in the case of acid-alcohol soluble casein and have found the ratio r_E/r_S to be 1.43. If we assume a similar ratio for the Van Slyke and Baker casein, we will have a molecular radius of 3.94×10^{-7} cm. and a corresponding diffusion constant, as calculated from Einstein's Law $D = \frac{RT}{N}\frac{1}{6\pi hr}$, of 5.41×10^{-7} cm. Solving the molecular weight equation with this diffusion value, we find the molecular weight of the bulk of the protein material of Van Slyke and Baker casein to be 100,300. This value corresponds very well with the molecular weight values 103,600 and 105,500, respectively, for serum globulin and phycocyan, which have been found to have S_{20° values of 5.57×10^{-13} and 5.59×10^{-13}, respectively. The S_{20° value we have found for the main protein component of Van Slyke and Baker casein is 5.56×10^{-13}, practically identical with the former of these last values. This S_{20° value, however, is no doubt somewhat high, as is also the molecular weight figure, due to the presence of the impurity of higher molecular weight, as we have mentioned before. There can be no doubt that the bulk of the casein prepared by Van Slyke and

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[5] Svedberg, "Colloid Chemistry," 2d ed., Chemical Catalog Co., New York, 1928, p. 164.

Baker's method has a molecular weight between 75,000 and 100,000. Attention is again called to the fact that Van Slyke and Baker casein does not consist of a single molecular species.

Effect of Heat on the Casein Molecule.—Inasmuch as other investigators have paid little or no attention to the temperature conditions that have been employed in the preparation of their protein solutions, we have thought it advisable to compare casein solutions that had been heated to 40° during their process of solution in phosphate buffer with casein solutions that had been prepared by dissolving in the same buffer in the cold and which have just been described.

In these experiments casein prepared by the method of Van Slyke and Baker was dissolved in the same phosphate buffer solution and with the same technique as previously described, except that the protein and solvent were, in the present case, subjected to a temperature of 40° for one hour while the protein was going into solution. This solution was then passed slowly through the milk separator, which was operated at a high speed, and the solution stored at 5° with a few drops of toluene as preservative.

In order to show clearly the range of size of the protein particles existing in this solution and their respective molecular weights after the above treatment, we have examined the solution by the sedimentation equilibrium method. This method has been described in detail elsewhere and it is sufficient here to state that the molecular weight is given by the relationship

$$M = \frac{2RT \ln (C_2/C_1)}{(1 - V\rho)(X_2^2 - X_1^2)\omega^2}$$

where M represents molecular weight, R the gas constant, T the absolute temperature, C_2 and C_1 the protein concentrations at the distances X_2 and X_1, respectively, from the center of rotation after equilibrium is attained, V the partial specific volume of the protein, ρ the density of the solvent and ω the angular velocity.

The results of a run with Van Slyke and Baker casein which had been heated for one hour at 40° are given in Table IV. It will be seen that the bulk of the protein in the cell corresponds closely to a molecular weight of 188,000 and at the bottom of the cell we have a heavier constituent of molecular weight 370,000. This latter appears to be the acid–alcohol soluble casein described in our former communication. There is no sign of any protein material in this solution having a molecular weight around 100,000, such as we find the bulk of Van Slyke and Baker casein to consist of when it has not been subjected to the action of heat. From this we must conclude that the protein of molecular weight between 75,000 and 100,000 has been entirely converted into a different and a larger molecule by the action of the applied heat. The data indicate that the molecule after the

TABLE IV

VAN SLYKE AND BAKER CASEIN SUBJECTED TO HEAT. SEDIMENTATION EQUILIBRIUM METHOD. PRELIMINARY DATA

Initial concentration, 0.95%; P_H, 6.8; thickness of cell. 0.20 cm.; T, 293°; speed 4430 r.p.m. ($\omega = 147.7\pi$); equilibrium time, 60 hrs.; illumination, Hg lamp with Br_2 and Cl_2 filters; Imperial Process photographic plates.

X_2, cm.	X_1, cm	C_2, %	C_1, %	M
5.85	5.80	1.643	1.289	373,700[a]
5.80	5.75	1.289	1.064	298,150[a]
5.75	5.70	1.064	0.9170	233,080[a]
5.70	5.65	0.9170	.8160	184,550
5.65	5.60	.8160	.7265	185,350
5.60	5.55	.7265	.6455	190,310
5.55	5.50	.6455	.5760	185,070
5.50	5.45	.5760	.5100	199,490
5.45	5.40	.5100	.4555	186,960
			Mean mol. wt.	188,620

[a] Excluded in calculating mean value of lighter species.

action of heat has at least twice the molecular weight that it had before such treatment. This suggests a polymerization or association of the molecules of molecular weight between 75,000 and 100,000 to form the larger molecules through the influence of heat. Our experiments do not show which of these suggested mechanisms is responsible for the changes in molecular weight which we have recorded. They do show, however, that in the case of casein, other factors remaining constant, the temperature at which the protein material is put into solution has a great influence on the state of the molecule.

It has often been noted that temperature changes and various other factors influenced certain physical properties of protein solutions. Such effects have been due largely to obscure causes and have been referred to as depending on "life history," etc., of the material in question. Evidence is here presented that in the case of casein the heat effect is a very definite one which results in at least doubling the molecular weight.[6]

Discussion of Results.—The experiments described in this paper with casein prepared from cow's milk by the method of Van Slyke and Baker have shown that this material is a mixture of protein substances of different molecular weight. Furthermore, samples from separate casein preparations made by this method of preparation, are shown to be different from each other, showing that not only a mixture of proteins is produced by the Van Slyke and Baker method, but a different mixture is to be found in different individual preparations. That little or no definite conclusions could be arrived at from researches based on such starting materials is entirely obvious.

[6] The authors are indebted to B. Sjogren for repeating and confirming our centrifuging results with the heated casein solutions described above.

There can be no doubt that the molecular weight of the main bulk of the protein separated by Van Slyke and Baker's method lies between 75,000 and 100,000.

In the equilibrium experiments where the casein solutions were subjected to a temperature of 40° while the moist casein was dissolving in the buffer solution, we have found that the protein of molecular weight between 75,000 and 100,000 has been altered to form larger molecules of molecular weight 188,000. That this represents an actual change in the molecules is evidenced from the fact that calculations of the specific sedimentation velocity of the 188,000 molecule yield an $S_{20°}$ value of 10.55 X 10^{-13} on the basis of a spherical molecule, and a similar value of 7.59×10^{-13} on the basis of a molecule of the same shape as the acid–alcohol soluble casein reported in the first paper. Neither of these values can be confused with or mistaken for the $S_{20°}$ value of 5.56×10^{-13} which we have obtained for the 75,000 to 100,000 weight molecule. We must be dealing, therefore, with another casein molecule in this casein which has been subjected to the influence of heat. In other words, the 100,000 molecule has been converted into the 188,000 weight type through the agency of heat. This change has been so complete that we do not find any of the 75,000 to 100,000 weight molecule even at the top of the sedimentation cell, where they would most certainly occur were any left unchanged in the solution.

Summary

1. Casein prepared by the method of Van Slyke and Baker has been examined at P_H 6.8 in phosphate buffer solutions at various protein concentrations by the centrifugal sedimentation velocity method, and found to consist of a mixture of protein substances of different molecular weight.

2. Different preparations made by this method were shown to be mixtures of proteins in different proportions. Not even a constant mixture was obtained by the Van Slyke and Baker method.

3. It was found that the bulk of the crude casein prepared by this method had a molecular weight between 75,000 and 100,000.

4. Crude casein subjected to a temperature of 40° during the time of dissolving in buffer solutions was found to have a molecular weight of 188,000 by the sedimentation equilibrium method. No molecules of molecular weight between 75,000 and 100,000 remained in the solution after this heat treatment.

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STUDIES ON POLYMERIZATION AND RING FORMATION. IV, ETHYLENE SUCCINATES

BY WALLACE H. CAROTHERS AND G. L. DOROUGH

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Ethylene succinate as a typical example of a condensation polymer[1] has been submitted to further study with the view of gaining more information in regard to its structure. The presence of the structural unit,[1] I, in this ester has been established by the methods used in its synthesis,[2,3] by its chemical behavior, and by its analytical composition.[2,3]

$$—O—CH_2—CH_2—O—OC—CH_2—CH_2—CO— \qquad (I)$$

Of the various polymeric forms described in this paper, the apparent molecular weights indicate average values of 6 and 23, respectively, for the number of structural units contained in each molecule of the lowest and highest polymers. It is assumed that these units are joined together in a linear fashion by real primary valences, as in II. Since it is very improbable that there are free valences at the ends of the resulting chains, the problem of the structure of these polymers resolves itself into finding whether the end valences are mutually saturated with the formation of very large rings or are saturated by univalent groups of some kind.

$$—O—(CH_2)_2—O—OC—(CH_2)_2—CO—O—(CH_2)_2—O—OC—(CH_2)_2—CO—O— \\ (CH_2)_2—O—OC—(CH_2)_2—CO—, \text{ etc.} \qquad (II)$$

Any of the reactions by which this ester is prepared offers the formal possibility of establishing either rings (closed chains) of 8, 16, 24, ...(8)*n* members or of open chains corresponding to each of these rings. The observed molecular weights indicate the presence of 50 to 180 atoms in each chain. This fact and the physical properties of the ethylene succinates indicate the absence of more than traces of rings of less than 32 members. Since the same theoretical considerations[4,1] which predict the improbability of the formation in bifunctional reactions of rings of 8 to 32 members apply *a fortiori* to still larger rings, an open chain seemed much more probable than a cyclic structure, and our efforts were directed toward the detection of the univalent groups which would constitute the ends of the open chains. We have proved the presence of such groups, and the open-chain structure for the polymeric ethylene succinates is clearly established.

Neutral Ethylene **Succinate.**—This ester is prepared by heating suc-

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[1] Carothers, THIS JOURNAL, 51, 2548 (1929).

[2] Vorlander, *Ann.*, 280, 167 (1894).

[3] Carothers and Arvin, THIS JOURNAL, 51, 2560 (1929).

[4] Mohr, J. *prakt.* Chem., 98, 348 (1918).

cinic acid with excess glycol at 180° until the distillation of water ceases and then removing the excess glycol by heating in high vacuum at 200–250°. The ester is purified by crystallization and melts at 102°.[5]

Its apparent molecular weight is about 3000.

If this ester is an open chain, its method of formation and its observed molecular weight would lead one to assign to it the structure III, and it

$$\text{H—[O—(CH}_2)_2\text{—O—OC—(CH}_2)_2\text{—CO—]}_{22}\text{—O—(CH}_2)_2\text{—OH} \qquad \text{(III)}$$

should therefore show the reactions of a dihydric alcohol. The possibility of applying to it many of the typical reactions for the detection of primary alcohol groups was excluded for one reason or another. Thus the presence of ester linkages excluded any reactions which might result to hydrolysis. The fact that the compound is hygroscopic and insoluble in ether made it useless to attempt to apply any such methods as the Zerewitinoff. The compound crystallizes from acetic anhydride and is apparently unchanged even on long boiling in this solvent in the presence of catalysts, but in so large a molecule acetylation might occur without any apparent change in physical properties, and the amount of acetic acid which would be liberated on hydrolysis of even a completely acetylated product would be so small as to make its estimation difficult. The ester reacts very slowly and incompletely with phosphorus tribromide.

Six grams of the ester heated for five hours in 30 cc. of boiling chloroform with 6 cc. of phosphorus tribromide after thorough washing and repeated crystallization was found to contain 0.58% Br.

The ester was also recovered apparently unchanged after treatment with phenyl and naphthyl isocyanates under various conditions. These failures appear to be due to a reluctance of the hydroxyl groups to react, and they are not altogether surprising in view of the diminished reactivity which is frequently associated with increased molecular size.

Reaction occurred completely in the expected sense with succinic and with p-bromobenzoic anhydrides at elevated temperatures. These reactions led to the dibasic acid which agreed in properties and composition with the Formula IV, and to a *p*-bromobenzoyl ester which agreed in composition with Formula V.

$$\text{HO—OC—(CH}_2)_2\text{—CO—[—O—(CH}_2)_2\text{—O—OC—(CH}_2)_2\text{—CO—]}_{23}\text{—OH} \qquad \text{(IV)}$$

$$p\text{-BrC}_6\text{H}_4\text{—CO—[—O—(CH}_2)_2\text{—O—OC—(CH}_2)_2\text{—CO—]}_{22}\text{—O—(CH}_2)_2\text{—O—OC—C}_6\text{H}_4\text{Br-}p \qquad \text{(V)}$$

Preparation of IV.—Twelve grams of neutral ethylene succinate was heated with 3 g. of succinic anhydride at 175–180° for three hours. The reaction mixture was washed three times with hot water, dried, precipitated from chloroform with ether and crystallized 6 times from acetone. Its properties identified it as the dibasic acid IV, which would be formed by the reaction of each hydroxyl group of III with one molecule of succinic anhydride.

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[5] Capillary tube melting point. See Carothers and Arvin, THIS JOURNAL, 51, 2560 (1929), for a description of the peculiar melting point behavior of this compound.

The ester III melted at 102°, had an apparent molecular weight of about 3000, was neutral and did not form a sodium salt. IV prepared from III melted at 98° and had an apparent molecular weight of 3110 (method of Menzies and Wright in ethylene chloride, observed values 3170, 3040) and a neutral equivalent of 1708. The action of sodium bicarbonate on IV led to a sodium salt which melted at 104° and contained 1.23% of sodium. The analytical data are given in Table I.

Preparation of Di-p-bromobenzoyl Derivative of **III.**—Two and one-half grams of III was heated for five hours with 0.75 g. of *p*-bromobenzoic anhydride at 175–185°. The reaction mixture was dissolved in chloroform and precipitated by ether, washed with hot water, dried and precipitated from acetone by ether. It melted at 93°. Analysis showed it to be the expected di-*p*-bromobenzoyl derivative, V, of III.

Anal. Calcd. for V as $C_{176}H_{172}O_{84}Br_2$: C, 49.30; H, 5.20; Br, 4.84. Found: C, 4947, 49.39; H, 5.59, 5.60; Br, 4.84, 5.01, 4.88, 4.91.

Acidic Ethylene Succinates.—If glycol and succinic acid would react completely in the proportions in which they are brought together, it would be possible to prepare chains of various lengths by using the glycol and acid in various ratios. In a number of experiments various excess amounts of succinic acid were allowed to react with glycol. The reactants were heated together at 180° until no more water was evolved and the temperature of the bath was then raised to 200–240° for one to five hours to make the reaction as complete as possible. Only traces of acid and glycol appeared in the distillates. The residues were always acidic and, when the excess of acid was large, always contained some unchanged succinic acid. Moreover, products of high molecular weight could be isolated from these residues even when the ratio of acid was as high as 2:1. This showed that under the conditions of these experiments complete control of the length of the chain produced was not possible by adjustment of the ratios of the reactants. On the other hand, this factor had some influence in controlling the lengths of these chains, and by making use of such control as it offered, together with fractional crystallization, it was possible to isolate samples of material representing chains of various lengths, each of which was quite homogeneous in its physical behavior. A comparison of the analytical data and molecular weights for these acidic ethylene succinates clearly indicates that their structure may be represented by VI, in which x has various average values for different fractions.

$$HO{-}OC{-}(CH_2)_2{-}CO{-}[{-}O{-}(CH_2)_2{-}O{-}OC{-}(CH_2)_2{-}CO{-}]_x{-}OH \quad \text{(VI)}$$

VIa, $x = 6$ VIb, $x = 9$ VIc, $x = 12$

Preparation of VI, a, b and c.—Ethylene glycol, 41 g., and succinic acid, 93.5 g. (20% excess), were heated at 200–210° for four hours, and the residual water was then removed as completely as possible by heating in *vacuo* The residue was dissolved in chloroform and precipitated with ether. The powder which resulted from the drying of this precipitate weighed 92.2 g. and melted at 87.5–90°. It was extracted several times with boiling water. The residue (59 g.) was dissolved in chloroform and precipitated by ether. It melted at 90°. This constituted fraction VIc. The hot aqueous extracts on cooling deposited 11 g. of solid which after drying melted at 73–74°.

In another similar experiment the acid and glycol were heated for two hours at 190–210° under ordinary pressure, and then immediately extracted several times with boiling water (3 × 300 cc.). The residue amounted to 10.5 g. After solution in chloroform and precipitation by ether, it melted at 82–83°. This constituted fraction VIb. On cooling, the aqueous extract deposited considerable white solid. This after precipitation from chloroform by ether melted at 73°. This material together with the fraction from the previous experiment melting at the same temperature constituted fraction VIa. By evaporation of the aqueous extracts from this experiment there was obtained another fraction melting at 86°. The analytical data for this fraction indicated that it lay between the 73° and the 82° fractions.

Fraction IV was prepared from III in the manner already indicated.

The analytical data for these fractions (see Table I) indicate that we are here dealing with a polymeric series in which the average values for the degree of polymerization vary from 6 up to 23. These fractions closely resemble each other in physical properties: they have the same appearance under the microscope, and they show similar solubility relations. All the fractions are soluble in cold chloroform and in hot 50% alcohol. The lowest fraction is quite soluble in hot water and the higher fractions only very slightly soluble. The melting points rise with increasing degree of polymerization.

All these fractions form sodium salts on treatment with sodium bicarbonate, and these resemble very closely in properties the acids from which they are derived. Thus they are readily soluble in cold chloroform and in warm acetone. They are only slightly soluble in cold water. All of them, however, are readily soluble in warm water, and in this respect the higher members are sharply differentiated from the corresponding acids. The magnitude of the change in properties which is produced by the transformation of the slightly polar carboxyl group into the completely polar sodium salt will be expected to vary with the size of the chains to which these groups are attached, but we found it somewhat surprising, nevertheless, that these sodium salts should melt only a few degrees above the melting points of the corresponding acids. This difference diminishes continuously with the increase in length of the chain and in the highest polymer, IV, amounts to only 6°.

The general plan of the structure of these acid esters is clearly established by the formation of the sodium salts. Attempts to prepare other derivatives from acids met with little success. Treatment with thionyl chloride and with phosphorus pentachloride under various conditions furnished products which contained chlorine, but it could not be established that these materials were really acid chlorides. Attempts to prepare amides by heating the sodium salts of the acids with *p*-toluidine hydrochloride led to the formation of N-*p*-tolyl succinimide. Heating the sodium salts with p-bromophenacyl bromide led to the formation of derivatives, but these contained less than the calculated amount of bromine. Thus the sodium salt of VIa led to a derivative, m. p. 73°, containing 8.66% of bromine, while the calculated value for a di-(*p*-bromophenacyl) ester of VIa is 11.61% Br. Similarly, the sodium salt of VIc led to a p-bromophenacyl derivative containing 4.12 instead of the calculated 7.13% of bromine.

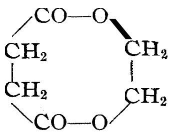
TABLE I

ACIDIC ETHYLENE SUCCINATES

Sample	M. p., °C.	Neut. equiv.	Mol wt. calcd. from neut. equiv.	Mol wt. found in boiling ethylene chloride	X = structural units per molecule	Mol. wt. calcd. from formula
VIa	73	508	1016	1070	6	982
VIb	82	672	1344	1380	9	1414
VIc	90	898	1795	1582	12	1847
IV	98	1708	3417	3110	23	3432

Anal calcd., % C	H	Anal found, % C		H		Sodium salt M p, °C.	Anal., sodium Calcd.	Found
48.86	5.44	48.42	48.58	5.57	5.29	91	4.48	4.26
49.22	5.56	48.84	48.88	5.74	5.62	97	3.16	3.13
49.38	5.57	49.34	49.37	5.86	5.81	100	2.43	2.29
49.66	5.58	49.41	49.44	5.70	5.69	104	1.32	1.23

Mechanism of the Formation of Ethylene Succinate.—The formation of an open-chain poly-ester of the type exemplified by II might occur in either one of two ways. (1) The cyclic monomeric ester VII might first be formed, and this might then undergo A polymerization (self-addition) with the formation of II. (2) II might be formed directly from the acid and the glycol (C polymerization) by a series of successive reactions. That poly-esters of this general type may be formed by the first mechanism is clearly indicated by the fact[6] that the monomeric form of trimethylene carbonate can be isolated by the distillation of its polymer, and, by heating, the monomer can be changed to the polymeric form. This is also true of other poly-esters, but, so far as our information extends now, only of those in which the monomer is a 6-membered ring. The 5-ring esters do not polymerize; the poly-esters whose monomers would be larger-than-6-rings are not depolymerized; and, although monomers of this type are known[7] and are stable, none of them has ever been prepared by a bi-functional reaction. The general theory underlying these facts has already been discussed.[1,6]



VII

The evidence that ethylene succinate is formed by Mechanism 2 (C polymerization) rather than 1 is fairly conclusive. Experimental evidence

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[6] Carothers and Van Natta, THIS JOURNAL, 52, 314 (1930).

[7] Ruzicka and Stoll, *Helv. Chim. Acta*, 11, 1159 (1928).

in support of Mechanism 2 may be found in the fact that the molecules of ethylene succinate are open chains with functional groups at the ends. The supposition that the monomeric ring VII is first formed involves the tacit assumption that 8-rings are readily formed, but are unstable, whereas fact and theory alike indicate that such rings are formed only with great difficulty, but are stable when they have been formed. We have made a good many attempts to isolate the monomeric 8-ring, VII. All of these attempts have failed, and all of the observations which we have made are best interpreted on the assumption that the long chains are built up by a series of successive reactions and that rings are not formed at any stage of the process. Some light is thrown at one or two points on the details of the mechanism of the reaction by the following observations.

When glycol was allowed to react with succinic acid in the proportions of 1 to 2 moles, the product was found to be a mixture composed chiefly of unchanged succinic acid and poly-ester of fairly high molecular weight. The compound, $HO—OC—(CH_2)_2—CO—O—(CH_2)_2—O—OC—(CH_2)_2—CO—OH$, which might be expected to form under these stoichiometrical conditions was not found.

Neutral ethylene succinate was prepared by heating the acid with excess glycol and, after some time, distilling off the excess glycol as completely as possible at high temperature and under greatly reduced pressure. Under these conditions the formation of some di-β-hydroxyethyl succinate, VIII, might be expected. This ester was in fact formed, and it distilled

$$HO—(CH_2)_2—O—OC—(CH_2)_2—CO—O—(CH_2)_2—OH \qquad \text{(VIII)}$$

out of the reaction mixture when this was heatkd in *vacuo.* It was obtained in a state of approximate purity by redistillation in a carefully cleaned all-glass apparatus under high vacuum.

Di-(β-hydroxyethyl)-succinate.—Sixty-two grams of ethylene glycol (1 mole) and 39.3 g. of succinic acid ($^1/_3$ mole) in a pyrex Claisen flask fitted with ground-glass stoppers and provided with a receiver were heated for six hours by means of an oil-bath at 174–180°; 8.8 g. of water, b. p. 100–102°, n^{28}_{D} 1.3323, collected in the receiver. The residue was heated in vacuo finally to a temperature of 250° at 0.015 mm., until distillation ceased. The residue was a pale yellow viscous liquid which readily solidified on cooling. It was dissolved in 100 cc. of warm chloroform and precipitated as a powder by the addition of 250 cc. of benzene. After drying, this powder weighed 36 g (0.25 *g.* equivalent). Its instantaneous melting point was 98° and its slow melting point 105.5". The distillates were redistilled and yielded 9.97 g. or 0.648 mole of water, 33.9 g. or 0.548 mole of glycol and 14.5 *g.* or 0.07 mole of di-(β-hydroxyethyl) succinate. The total esters (0.7 mole + 0.25 *g.* equivalent) accounted for 0.32 mole of the 0.333 mole of succinic acid used, and these esters plus the glycol recovered accounted for 94.6% of the glycol used, while the water isolated was 87.5% of the calculated amount.

The di-(β-hydroxyethyl) succinate was never isolated in a state of purity. When distilled in a carefully cleaned all-glass (pyrex) Claisen flask, it boiled at 176–180° at 0.001 mm. as a colorless viscous liquid, leaving only a trace of residue.

Anal. Calcd. for $C_{10}H_{14}O_6$: C, 46.58; H, 6.88. Pound: C, 45.76, 45.70; H, 6.86, 6.95.

Treatment with *p*-nitrobenzoyl chloride in pyridine yielded a di-(*p*-nitrobenzoate) as white needles from alcohol; m. p. 90–91°.

Anal. Calcd. for $C_{22}H_{20}O_{12}N_2$: C, 52.35; H, 3 97. Found: C, 52.36, 52.36; H, 4.19, 4.14.

The di-(phenylurethan) formed by the action of phenyl isocyanate on di-(β-hydroxyethyl) succinate and crystallized from a mixture of benzene and petroleum ether melted at 113°.

Anal. Calcd. for $C_{22}H_{24}O_8N_2$: C, 59.45; H, 5.41. Found: C, 59.40, 59.56; H, 5.53, 5.52.

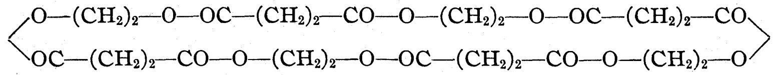
When heated slowly in *vacuo* di-β-hydroxyethyl succinate was completely converted into neutral (polymeric) ethylene succinate and ethylene glycol, the former appearing in the distillate and the latter remaining in the distilling flask.[7] This process evidently involves an ester interchange: glycol is eliminated between two molecules of the dihydroxy ester with the formation of a new dihydroxy ester containing two of the structural units of ethylene succinate. Repetition of this process finally results in such a molecule as III. It is evident that so long as one of the products of a possible ester interchange can be eliminated in this way, no merely stoichiometrical factors can set up a limit to the length of the molecules which might be produced. Nevertheless a fairly definite limit exists: polyintermolecular esterification has never led us to molecules of greater average length than about 200 atoms. No doubt various factors are involved in this point. There can be no question that the reactivity of functional groups diminishes with the size of the molecules which contain them. It is apparently this factor which accounts for the failure of the ester III to react with many of the typical reagents for hydroxyl groups. Moreover, as Staudinger has frequently emphasized,[8] the thermal stability of molecules must diminish with increase in their size. These two factors act in opposition. To force the completion of the reaction between succinic acid and glycol we have used high temperature (250°) to increase reaction velocity and high vacuum to remove the water as completely as possible. The ester produced under these conditions has a molecular weight of about 3000. It is interesting to observe that in the thermal polymerization of styrene the product formed at 250° also has an apparent molecular weight of about 3000, while the polystyrenes formed at lower temperatures have much higher molecular weights. And so also the A polymerization of trimethylene carbonate described in the previous paper,[6] although it also involves an ester interchange, leads to a poly-ester with a molecular weight considerably above 3000, since the reaction consists merely in self-addition and proceeds rapidly at 100°.

[8] See Staudinger, *Ber.*, 59, 3019 (1926).

Dimeric Ethylene Succinate.—Tilitschejew[9] has reported the isolation of a new ethylene succinate from the volatile materials formed by heating the product of the action of succinic acid on glycol (m. p. 88–89°) to 340–390° under 3–4 mm. pressure. The new product was distinguished from the usual form not only by its different melting point (129–130°), but by its definite macrocrystallinity. Cryoscopic data on acetic acid solutions of the new ethylene succinate indicated a double formula and, since Vorlander had already reported[10] that the old form was dimeric, Tilitschejew regarded his new ester as an isomer of the old. It has now been established that the usual form of ethylene succinate is not dimeric, but much more highly polymeric; the new compound cannot, therefore, be simply an isomer of the old. Aside from this, however, repetition of Tilitschejew's experiments has completely verified the correctness of his claims as to the nature of the new compound. It crystallizes in thin plates melting sharply at 130°. The analytical data clearly indicate that it is dimeric ethylene succinate.

Anal. Calcd. for $(C_6H_8O_4)_2$: C, 50.00; H, 5.50; mol. **wt.,** 288; saponification equivalent, 72. Found: C, 49.85, 50.00; H, 5.60, 5.57; mol. wt., in boiling ethylene chloride, 302, 299; in freezing benzene 279; saponification equivalent, 71.97, 71.95, 71.66.

Attempts to partially saponify this ester were unsuccessful—a part of the ester was recovered unchanged and the remainder was degraded to sodium succinate and glycol. Nevertheless, it seems fairly certain that this compound is the 16-membered ring, IX. No alternative formula seems



$$\begin{matrix} O-(CH_2)_2-O-OC-(CH_2)_2-CO-O-(CH_2)_2-O-OC-(CH_2)_2-CO \\ OC-(CH_2)_2-CO-O-(CH_2)_2-O-OC-(CH_2)_2-CO-O-(CH_2)_2-O \end{matrix}$$

(IX)

plausible. It is very improbable that this compound is present as such in the polymeric ester from which it is prepared. The dimer is quite soluble in hot absolute alcohol; the neutral polymer is quite insoluble. Continuous extraction of the polymer with hot absolute alcohol resulted in the solution of only a very small amount of material and this had the properties of the polymer not of the dimer. The dimer must therefore be formed during the process of thermal decomposition. The transformation of polymeric trimethylene carbonate into monomeric ethylene carbonate described in the previous paper[6] proceeds smoothly and practically quantitatively at about 200°. The formation of the dimeric tetramethylene carbonate, described in the same paper, and of dimeric ethylene succinate occurs only at a much higher temperature. Large amounts of gaseous and liquid products are formed as well as considerable

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[9] Tilitschejew, *J. Russ. Phys.-Chem. Soc.*, *57*, 143–150 (1925); *Chem. Zentr.*, I, 2667 (1926).

[10] Vorlander, *Ann.*, 280, 167 (1894).

carbonaceous residue. The yields of the dimers are quite small, *e. g.*, 3–4% of the theoretical under the best conditions (Tilitschejew, however, reports 5.5%). In these respects the reaction resembles that used by Ruzicka for the preparation of the large cyclic ketones.[11] As yet we have not succeeded in isolating any monomeric ethylene succinate from the products of this reaction.

Ethylene Succinate and the Association Theory of High Polymers.—The discussion in this and the previous papers will, it is hoped, have amply demonstrated the adequacy of the ordinary structural theory of organic chemistry to deal with the poly-esters, a fairly complicated class of high polymers.

A possible explanation of the structure of the poly-esters which has not yet been considered is the following. The chemical unit or molecule of ethylene succinate is the monomeric 8-ring, VII. Because of the great strains in this structure, or for some other reason, it exhibits exceptionally strong residual or lattice forces, so that the osmotic unit becomes an aggregate of a great many of these ultimate chemical units. There is such a complete lack of any general theoretical justification for this view that there would be no need to consider it in connection with the poly-esters were it not that in the field of natural polymers such as cellulose, rubber, etc., in various slightly differing forms it has been defended at great length by so many investigators.[12]

Among the many facts which are quite incompatible with any association theory of the structure of poly-esters, the following deserve special mention.

(1) All of the known cyclic esters containing larger-than-6-rings are stable substances with definite properties corresponding with their simple formulas. They do not show any tendency to associate in solution.

(2) The polymeric esters corresponding to these monomers show no tendency to dissociate.

(3) In the polymeric ethylene succinates the chemical and osmotic units have been shown to be identical within the limits of experimental error, i. *e., ebullioscopic data give the same values for the molecular weights that are given by the determination of hydroxyl or carboxyl.*

The association theory is not clearly enough defined to permit any more crucial tests than these, but the following experiment at any rate agrees with these in the conclusions to which it leads.

If two different association polymers $(A)_n$ and $(B)_m$ are mixed in solution or in the liquid state so that they constitute a single phase, then

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[11] Ruzicka and co-workers, *Helv. Chim. Acta*, **9**, 230, 249, 339, 389, 399, 499, 715, 1008 (1926); **10**, 695 (1927); **11**, 496, 670, 686, 1159, 1174 (1928).

[12] See for example Bergman, Knehe and Lippmann, *Ann.*, **458**, 93 (1927); Hess, Trogus and Friese, *ibid.*, **466**, 80 (1928); Schlubach and Elsner, *Ber.*, **61**, 2358 (1928); Pummerer, Nielsen and Gündel, *ibid*, **60**, 2167 (1927).

since $(\mathrm{A})n \rightleftarrows n\mathrm{A}$ and $(\mathrm{B})m \rightleftarrows m\mathrm{B}$, the resulting mixture should be composed at least in part of (AB),.

Ethylene sebacate (m. p. 78°) and ethylene succinate (m. p. 103°) were melted together and thoroughly mixed. After cooling, the mass was extracted with benzene, which is a solvent for the sebacate but not for the succinate. The residue melted at 103° (unchanged succinate). To the benzene solution petroleum ether was added; the precipitated solid melted at 78–79° (unchanged sebacate). An ester was prepared by the action of glycol on equivalent amounts of succinic and sebacic acids. This was quite different in its properties from either the succinate or sebacate and it was homogeneous in its solubility behavior (m. p. 38–40°; mol. wt. 1540). This demonstrates the existence of a mixed polymer and the absence of any reversible relationship of association between it and the two corresponding simple polymers.

In the 6-ring esters a reversible relationship exists between the monomeric and polymeric forms, and some of the statements made above do not apply to these polymers. But it is possible, nevertheless, to account satisfactorily for the behavior of these esters without the assumption of any special or peculiar kinds of valence.[6]

The view that the ordinary structural theory of organic chemistry is adequate to deal with high polymers has been now for several years ably defended by Staudinger and his collaborators,[13] and recently the same view has been applied in a brilliant fashion to such natural polymers as cellulose, rubber, silk fibroin, etc., by Meyer and Mark.[14] So far as the minor differences[15] in the views of these two groups of investigators are concerned, our own experiments on poly-esters incline us to favor those of Staudinger. That is, we can find no real objection to referring to primary valence chains as molecules, and among the polyesters these molecules are experimentally identical with the osmotic units of their solutions.

The writers are indebted to Mr. W. H. Taylor for the molecular weight determinations and to Mr. G. A. Jones for the determinations of carbon and hydrogen.

Summary

The polymeric ethylene succinate previously described is shown to be a long chain made up of the recurring unit —O—(CH$_2$)$_2$—O—CO—

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[13] Staudinger and co-workers, *Helv. Chim. Acta*, 5, 785 (1922); 7, 23, 842 (1924); 8, 41, 65, 67 (1925); 9, 529 (1926); 11, 1047, 1052 (1928); *Ber.*, 53, 1073 (1920); 57, 1203 (1924); 60, 1782 (1927); 59, 3019 (1926); 61, 2427 (1928); 62, 241, 263, 442 (1929); *Ann.*, 447, 97, 110 (1926); 467, 73 (1928); *Z. physik. Chem.*, 126, 425 (1927); *Kautschuk*, 237 (1927); *Z. angew. Chem.*, 42, 37, 67 (1929); *Z. Krist.*, 70, 193 (1929).

[14] Meyer and Mark, *Ber.*, 61, 593, 1932, 1939 (1928); Meyer, *Naturwissenschaften*, 42, 790 (1928); *Z. angew. Chem.*, *41*, 935 (1928).

[15] Meyer, *Naturwissenschaften*, 17, 255 (1929).

$(CH_2)_2$—CO— and bearing hydroxyl groups at its **ends.** Acidic ethylene succinates made up of similar chains of various lengths and bearing carboxyl groups at their ends have been prepared. Molecular weight determinations of these esters based on ebullioscopic measurements agree with those based on chemical evidence (estimation of hydroxyl or carboxyl).

A study of the ethylene succinate prepared by Tilitschejew verifies his claim that it is dimeric, and this ester is undoubtedly a 16-membered ring.

WILMINGTON, DELAWARE

[CONTRIBUTION NO. 55 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

THE RELATIVE RATES OF ABSORPTION OF THE GASEOUS OLEFINS INTO SULFURIC ACID AT 25°[1]

BY HAROLD S. DAVIS[2] AND REUBEN SCHULER[3]

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This paper deals with measurements of the rates at which the gaseous olefins and the vapors of some liquid olefins are absorbed by sulfuric acid of various concentrations at 25°.

The quantity of acid used was always much larger than the molecular equivalent of the amount of olefin taken so that the data apply only to sulfuric acid in the initial stages of saturation, where its character was not perceptibly changed by dissolved olefin reaction products. Thus the absorptions were of the type which take place in gas analysis pipets except that they were carried out at constant volume instead of at constant pressure.

Apparatus.—The apparatus employed to measure the rates of absorption (Fig. 1) consisted essentially of a cylindrical glass reaction chamber connected to a glass manometer tube dipping in mercury. A measured volume of the olefin gas was introduced into the evacuated chamber which contained sulfuric acid. The progress of the absorption was followed by recording the gaseous pressure shown by the height of mercury in the manometer tube at successive periods of time. When desired the chamber could be turned on its major axis at a definite number of rotations per minute (r.p.m.), the manometer tube turning with it. A flexible piece

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[1] This paper contains results obtained in an investigation on "The Relative Rates of Reaction of the Olefins" listed as Project No. 19 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

[2] Director and Research Associate, Fellowship No. 19.

[3] Junior Research Fellow, Fellowship No. 19.

of rubber tubing connected the two, and a stopcock isolated the chamber between readings.

Three absorption chambers were used during the course of the experiments. The inside dimensions of Nos. 2 and 3 used in the final experiments were: length 15.9 cm., diameter 5.1 cm., volumes 289 and 284 cc., respectively, including the connecting tubes. All three were made from standard 50 × 400-mm. pyrex test-tubes.

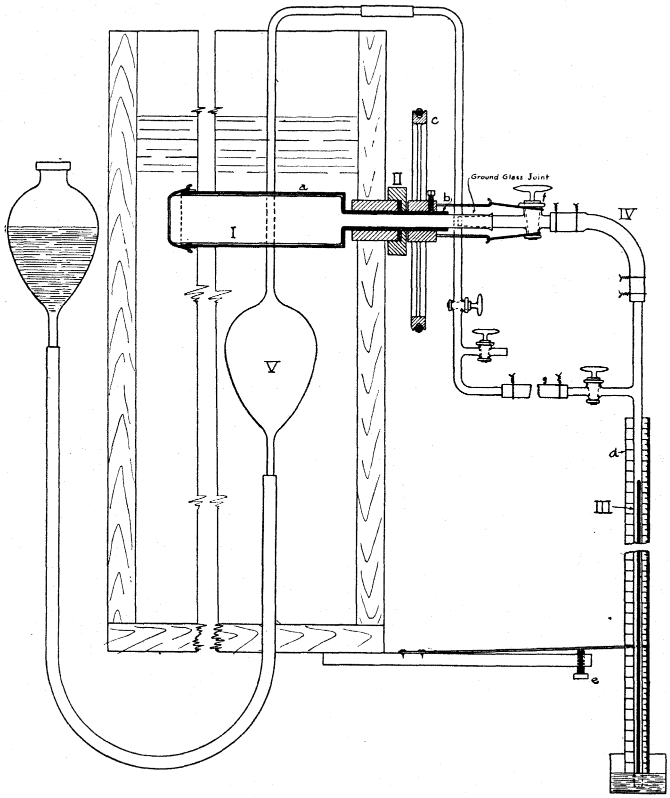

Fig. 1.—Apparatus for measuring the rate of absorption of an olefin gas into sulfuric acid. I.—Cylindrical glass reaction chamber, capacity 289 cc., in brass jacket "a," immersed in water-bath at *25".* 11.—Water-tight stuffing box through which passes exit tube "b" of brass jacket to driving wheel "c." 111.—Manometer tube dipping into mercury with a calibrated meter stick "d" adjusted to changing mercury level in cup by screw "e." IV.—Pressure tubing between chamber rotating horizontally and manometer rotating vertically. V.—Reservoir bulb for known volume of olefin gas to be introduced into reaction chamber "I" by mercury displacement.

Experimental Procedure.—Numerous preliminary experiments (1–12)

Table II, were necessary in order to develop our technique. These preliminary experiments contain, necessarily, many errors but they also contain material of such value that they have been included in the table of collected results.

The following discussion of the errors which were detected and of the methods used to overcome them throws light on the entire procedure. (1) In the preliminary experiments, the volume of the olefin gas was not measured before it was allowed to flow into the evacuated reaction chamber. Accordingly, it was not possible to gage the quantity absorbed by the liquid before the first pressure reading was taken. In the final experiments a definite volume of olefin gas, measured at atmospheric pressure and 25° in the reservoir bulb (V) was introduced into the evacuated chamber. From tests made with air and mercury in place of the olefin and the sulfuric acid, respectively, the pressure which the olefin gas would give in the reaction chamber if none dissolved in the acid was found. This calculated value represented the pressure reading at the beginning of an absorption, *i. e.*, $t = 0$. In no case was there any evidence of a rapid initial absorption which might have been attributed to physical solution of the gas in the acid.

(2) In the preliminary experiments care was not taken, during the addition of the acid, to prevent wetting the side walls and the ends of the chamber above the final level of the acid. However it soon became evident that a thin film of acid on the glass was, for a limited period of time, as effective for absorption as a similar area on the main body of the liquid. This error undoubtedly accounts for the wide variations in the preliminary results where the absorptions were measured with the chamber at rest [r.p.m. = 0]. In the final series the chamber was put in place as shown in the figure with the ground-glass joint open. The sulfuric acid was then poured into the center through a small funnel with a long bent stem. In this way wetting of the walls was largely avoided.

(3) Reaction chamber No. 1 was used in the preliminary experiments. It wobbled a little during rotation so that the sides were wetted unevenly and little waves were produced on the acid surface. Further, it had rounded ends, like an ordinary test-tube, from which at high speeds of rotation (100–200 r.p.m.) the acid drew away. Chambers 2 and 3 used in the final experiments were fitted inside a brass jacket which had been carefully centered to run true. Wobbling was thus cut down. Furthermore, their ends were flattened as much as possible which minimized, although it did not entirely eliminate, the errors caused by the round ends of No. 1.

(4) In the preliminary experiments no stopcock existed between the chamber and the rubber tube so that part of the olefin might have been absorbed, not into the acid but into the rubber. However, an analysis of the data shows that this error was much smaller than might have been expected. In all fast experiments it was negligible. For Expts. 50–80 a stopcock (F) was placed between the chamber and the rubber connection (IV). It was kept closed except when a pressure reading was taken. Any olefin in the manometer tube itself was removed by evacuating shortly after the start and replaced by air. The resulting apparatus held the olefin in the chamber out of contact with the rubber and even those absorptions could be safely followed which were so slow that they required several days for completion.

The Acid Surfaces and the Effects of Rotation.—Numerous experiments were carried out with the chamber at rest (r.p m. = 0). On rotation a fairly thick layer of acid was carried up one side. Part of this flowed back again but a thin film passed on to the other side. Here it met the surface layer of the liquid, which curved down several millimeters, and both were drawn under the liquid. Thus the surface of the film on the glass and that of the liquid itself were continuously renewed during rotation. A considerable mixing in the liquid also took place. If less than 10 cc. was used, the acid did not wet the surface uniformly on rotation but tended to form pools especially at high speeds. In the final experiments *20* cc. was used. Here the area of the film formed by rotation was nearly four times that of the liquid surface proper. Estimates were made of the average thickness of the acid films on the glass. This was done by measuring the change in the surface width of the acid, colored by purpurogallin, produced by rotation, and calculating its corresponding change in volume. For *70%* sulfuric acid the thickness was 0.1 to 0.3 mm., increasing with the speed of rotation. For concentrated acid it was somewhat greater.

Thin as these films were, they were thicker than the layers containing acid molecularly equivalent to all the gaseous olefins in the chamber, which were calculated to be only 0.04 mm. thick for *70%* acid and *0.023* mm. for concentrated.

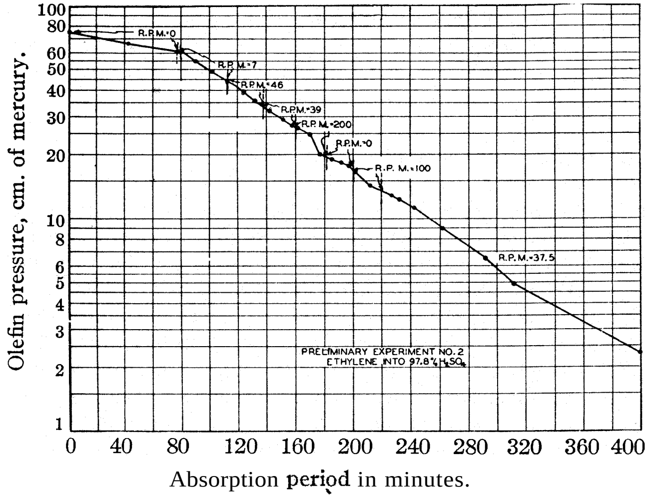

Fig. 2.

Calculations.—The actual variables measured in each experiment were (1) the length of the absorption period and (2) the gaseous pressure of the olefin. An examination of the absorption curves in Figs. 2 to 9, which are plotted on semi-logarithmic paper, shows that they tend to form straight lines over the greater part of the absorption. (The logarithm paper exaggerates the variations in the last period of absorption just as Mercator's projection makes Greenland seem larger than the United States on the map. Although the lower cycle is equal in width to the upper cycle, its range of values is only one-tenth.) That is, the logarithm of the olefin pressure decreased uniformly in proportion to the length of the absorption period and for each experiment the factor $1/t \ln 1/(1 - X)$ gave a fairly constant value of K (where X was the fraction of the olefin dissolved).

The magnitude of K was independent of the partial pressure of the gas and of the time of contact, To this extent its values are characteristic for the absorptions of the separate olefins.

Illustrative Calculations.—Preliminary experiment No. 2 (Fig. 2).

The absorption was followed for the first seventy-seven minutes with the chamber at rest. A straight edge placed on the absorption curve shows that it is sloping quite uniformly. The pressure would reach half value (37 cm.) in 300 min. Accordingly, K (for r.p.m. = 0) = $1/300 \times 60 \ln (1)/(1 - 0.5) = 0.39 \times 10^{-4}$.

The chamber was then rotated steadily at the rate of seven turns per minute. The absorption rate at once increased, due, as will presently appear, to the absorbing power of the acid film now formed on the glass surfaces. Nor was the rate much affected by a change in the speed of rotation. The variations in the slope seem to have been caused by experimental errors. (See discussion above of preliminary results.) As a whole, this absorption curve, for the tube rotating, lies around a straight line of such a slope that the pressure at any time would reach half value in about 70 min. Accordingly, K (chamber rotating) = $1/(70 \times 60) \times 0.693 = 1.65 \times 10^{-4}$.

In order to compare the absorption rates in cases where different areas of acid surface were exposed, or where different volumes of gas were used, it was found convenient to calculate from K in each case *a specific* ***absorption coefficient*** *C* which may be defined as the proportional change in volume at constant pressure which would take place in an infinitesimally short time when 1 cc. of the gas was in contact with 1 sq. cm. of an acid surface having the average absorbing power of the total acid surfaces

$$C = \frac{V\mathrm{d}p}{Ap\mathrm{d}t} \text{ at constant volume, or}$$

$$= \frac{dv}{A\mathrm{d}t} \text{ at constant pressure}$$

where A is the area of the absorbing surfaces.

At constant pressure, C is evidently equal to the average number of cc. of gas absorbed by 1 sq. cm. of acid surface in 1 sec.

The gas volumes for each experiment were easily found by subtracting from the total volume of the chamber, that of the acid used. The measure-

TABLE I

CALCULATED VALUES OF THE FACTOR *m* FOR THE VARIOUS EXPERIMENTAL CONDITIONS

	Chamber No. 1		Chamber No. 2		Chamber No. 3	
Vol. acid, cc.	At rest	Rotating	At rest	Rotating	At rest	Rotating
10	8.06	1.30				
20	6.11	1.25	5.50	1.12	5.40	1.09
25	5.69	1.23				
30	4.99	1.21				
90	2.73	0.887				

Completing the calculations started above for preliminary experiment No. 2 (ethylene + concd. H_2SO_4)

Chamber at rest $C = 0.39 \times 10^{-4} \times 4.99 = 1.95 \times 10^{-4}$

Chamber rotating $C = 1.65 \times 10^{-4} \times 1.21 = 1.99 \times 10^{-4}$

ments of the surface areas were more difficult: (a) the acid surface proper, area = width × average length. This constituted the whole absorbing surface at r.p.m. = 0. On rotation the following additional areas of absorbing surface were formed: (b) the acid film on the cylinder walls, area = average length × perimeter above acid surface, (c) the acid film on the ends, area = total area of ends − (area under acid + area not wetted)

$$C = mK \qquad \text{where } m = \frac{\text{Total cc. of gas}}{\text{Total area of absorbing surface}}$$

TABLE II

MEASUREMENTS OF THE RATES OF ABSORPTION OF OLEFIN GASES INTO SULFURIC ACID AT 25° (PRELIMINARY EXPERIMENTS)

Expt. no.		Olefin	Sulfuric acid Concn., %	Sulfuric acid Vol., cc.	Chamber	R.p.m.	$K \times 10^4$	$C \times 10^4$
(1)	I	Ethylene	97.8	30	1	0	0.53	2.7
	II	Ethylene	97.8	30	1	34	1.89	2.3
	III	Ethylene	97.8	30	1	0	0.29	1.5
	IV	Ethylene	97.8	30	1	34	1.73	2.1
(2)	I (Fig. 2)	Ethylene	97.8	30	1	0	0.39	1.95
	II to VII	Ethylene	97.8	30		7 to 200	1.65	1.99
(3)	I	Ethylene	97.8	10	1	0	0.25	1.97
	II	Ethylene	97.8	10	1	7	1.32	1.72
	III	Ethylene	97.8	10	1	38	1.55	2.02
	IV	Ethylene	97.8	10	1	100	1.91	2.48
	V	Ethylene	97.8	10	1	208	1.65	2.15
(4)	I	Ethylene	97.8	90	1	0	0.59	1.62
	II	Ethylene	97.8	90	1	44	2.28	2.02
	III	Ethylene	97.8	90	1	7.5	1.62	1.44
	IV	Ethylene	97.8	90	1	64.5	2.01	1.78
	V	Ethylene	97.8	90	1	180	2.00	1.77
(5)	I	Propene	70	30	1	0	0.17	0.85
	II	Propene	70	30	1	31	0.40	0.48
(6)	I	1-Butene (A)	70	30	1	0	0.13	0.62
	II	1-Butene (A)	70	30	1	31	0.39	0.47
(7)	I	Propene	97.8	30	1	31	530	640
	II	Propene	97.8	30	1	31		
	III	Propene	97.8	30	1	31		
	IV	Propene	97.8	30	1	31		
(8)	I	2-Butene (A)	70	30	1	0	[1.0]	[0.50]
	II	2-Butene (A)	70	30	1	31	[0.34]	[0.41]
(9)	I	1-Butene (B)	70	30	1	0	0.12	0.61
	II	1-Butene (B)	70	30	1	31	0.32	0.38
(10)	I	Isobutene	70	30	1	0	17.7	88.1
	II	Isobutene	70	30	1	31	48.8	59.0
(11)	I	2-Butene (B)	70	30	1	0	0.35	1.98
	II	2-Butene (B)	70	30	1	31	0.61	0.74
(12)	I	2-Butene (A)	70	30	1	0	0.19	1.08
	II	2-Butene (A)	70	30	1	31	0.58	0.73

TABLE II (Continued)

FINAL EXPERIMENTS

Expt.	Reference Fig.	Reference Curve	Olefin	Sulfuric acid Concn., %	Sulfuric acid Vol., cc.	Chamber	R p m	$K \times 10^4$	$C \times 10^4$
65	9	65	Ethylene	95.8	20	3	0	0.25	1.4
66	9	66	Ethylene	95.8	20	3	28	1.6	1.8
39	4	39	Ethylene	87	20	2	28	0.124	0.14
77	4	77	Ethylene	87	20	3	28	0.120	0.13
34	9	34	Ethylene	80	20	2	0	0.0016	0.0096
32	9	32	Ethylene	80	20	2	28	0.0110	0.014
80	9	80	Ethylene	80	20	3	28	0.0085	0.0094
[33			Ethylene	80	20	2	118	0.0115	0.013]
78			Ethylene	60	20	3	28	0.00014	0.00015
62	3	62	Propene	95.8	20	3	0	74	400
63			Propene	95.8	20	3	28	565	630
56	3	56	Propene	87	20	2	0	9.6	52.8
35	4	35	Propene	87	20	2	28	32.5	36.4
38	4	38	Propene	87	20	2	28	35.4	39.7
57	4	57	Propene	87	20	2	28	34.5	38.6
59	4	59	Propene	87	20	2	28	34.1	38.1
30	5	30	Propene	80	20	2	0	1.05	5.77
58	5	58	Propene	80	20	2	0	0.98	5.40
31	6	31	Propene	80	20	2	28	3.62	4.06
60	6	60	Propene	80	20	2	28	3.50	3.92
29	6	29	Propene	80	20	2	119	3.50	3.92
61	9	61	Propene	70	20	2	0	0.0748	0.41
64	8	64	Propene	70	20	3	28	0.480	0.53
79	8	79	Propene	60	20	3	28	0.115	0.126
67	3	67	1-Butene A	95.8	20	3	0	143	771
68			1-Butene A	95.8	20	3	28	1880	2050
69	3	69	1-Butene A	87	20	3	0	17.7	95.5
70	4	70	1-Butene A	87	20	3	28	60.6	66.1
73	5	73	1-Butene A	80	20	3	0	1.73	9.3
71	6	71	1-Butene A	80	20	3	28	3.7	4.0
74	3	74	2-Butene B	87	20	3	0	42.5	230
36	4	36	2-Butene B	87	20	2	28	124	139
37"	4	37	2-Butene B	87	20	2	28	123	138
27	5	27	2-Butene A	80	20	2	0	4.0	22.0
[75	5	75	2-Butene B	80	20	3	0	6.0	32.4]
28	6	28	2-Butene A	80	20	2	28	9.3	10.4
72	6	28	2-Butene B	80	20	3	28	9.8	10.7
[76	7	76	2-Butene B	70	20	3	0	0.15	0.81]
54	3	54	Isobutene	87	20	2	0	460	2530
55	4	55	Isobutene	87	20	2	28	2300	2500
18	5	18	Isobutene	80	20	2	0	36.5	201
19	5	19	Isobutene	80	20	2	0	36.5	201
20	6	20	Isobutene	80	20	2	28	575	642
21	6	21	Isobutene	80	20	2	28	560	624
22	7	22	Isobutene	70	20	2	0	11.0	60.5
23	7	23	Isobutene	70	20	2	0	10.9	59.9
50	7	50	Isobutene	70	20	2	0	10.25	56.4

TABLE II (Concluded)

Expt	Reference Fig	Reference Curve	Olefin	Sulfuric acid Concn, %	Sulfuric acid Vol, cc.	Chamber	R p m	$K \times 10^4$	$C \times 10^4$
24	8	24	Isobutene	70	20	2	28	53 5	59.9
25	8	25	Isobutene	70	20	2	28	52 3	58.6
51	8	51	Isobutene	70	20	2	28	49.0	55.0
26	8	26	Isobutene	70	20	2	119	46	51.6
52	7	52	Isobutene	60	20	2	0	2 67	14.7
53	8	53	Isobutene	60	20	2	28	8 66	9.7
40			Propene 77% + oxygen 23%	87	20	2	28	35.7	39.8
41			Ethene 50.4% + propene 49.6%	87	20	2	28	35.7	39.9
42	.	..	Isopropyl-	70	20	2	28	0.248	0.278
47	7	47	ethene	70	20	2	0	0 132	0.730
43	8	43	Trimethylethene	70	20	2	28	68 5	76.4
44			Trimethylethene 3 8% + air 96 2%	70	20	2	28	72 4	80.7
45			Trimethylethene	80	20	2	28	2111	2353
46			Trimethylethene	80	20	2	0	120	660

[a] The olefin was first exposed to ultraviolet light for 9 hrs.

TABLE III

COLLECTED SPECIFIC ABSORPTION COEFFICIENTS PER UNIT AREA ($C \times 10^4$) FOR THE GASEOUS OLEFINS INTO SULFURIC ACID IN A ROTATING CHAMBER AT 25°

The data in Table III represent the average values from the final experiments 18–80 in Table II with the following exceptions: (a) 1-butene and 2-butene into 70% H_2SO_4 were calculated from the preliminary experiments 1–18; (b) isobutene into 70% acid at 28 r.p.m. was derived from two preliminary experiments and three final; *(c)* the results from Expts. 33, 75 and 76 have been excluded

Concn. of acid.	95.8%		87%		80%			70%			60%	
R.p.m.	0	28	0	28	0	28	119	0	28–31	119	0	28
Ethylene	1.4	1.8	..	0.135	0.01	0.012	0.013	...	...	..	..	0.00015
Propene	400	630	52.8	38.2	5.58	3.99	3.92	0.412	0.526	. . .		0.126
1-Butene	771	2050	95.5	66.1	9.3	4.0	. .	0.619	0.429	. . . .		
2-Butene	...	..	230	138	22.0	10.5	...	1.53	0.742	. . . .		
Isobutene	...	..	2530	2500	201	633	...	58.9	57.8	51 6	14.7	9.7

TABLE IV

RATIOS OF THE ABSORPTION RATES OF THE GASEOUS OLEFINS INTO SULFURIC ACID AT 25°

Sulfuric acid.	95.8%				80%			70%		60%
R.p.m.	0	28	0		0	28	119	0	28 to 31	28
Propene/ethylene	288	350	...	283	550	362	305			840
1-Butene/propene	1.9	3.2	1.8	1.7	1.7	1.0		1.5	0.82	
2-Butene/propene			4.3	3.6	3.9	2.6		3.7	1.4	
*Iso*butene/propene			48	65	36	160		135	112	77
2-Butene/1-butene			2.4	2.1	2.3	2.6		2.5	1.7	
*Iso*butene/2-butene			20.9	18.1	9.2	61.6		36.5	80	

Discussion of Data

Reliability of the Measurements.—An examination of the figures shows that the absorption curves for check experiments usually lie very close to each other. The average deviation of K from the mean in 22 experiments in nine different types of absorptions was 1.6% (excluding Nos. 27 and 75 for 2-butene, where the deviation was 19%).

The Effects **of** Changes in the Rate of Rotation and in **the** Quantity of **Acid** Used.—For ethylene these effects are shown by Table VI.

TABLE V

EXPERIMENTAL RESULTS

The solutions of sulfuric acid were prepared from C. P. material and their concentrations were checked by titration

Olefin	Method of preparation[a]	B. p., °C.	F. p.,[b] °C.
Ethylene	"Refined" ethylene purchased from a well-known firm	......	...
Propene	Isopropanol and phosphorus pentoxide	−47.3 at 770 mm.	.....
1-Butene (A)	n-Butyl iodide and alcoholic potash	−6.0–−5.8	....
1-Butene (B)	Dehydration of n-butanol over alumina	−6.3–−5.1	.....
2-Butene (A)	*Sec.*-butyl iodide and alcoholic potash	1.8–2.2	−113
2-Butene (B)	2-Butanol and phosphoric acid	1.5–1.7	−122
Isobutene	*Tert.*-butanol and oxalic acid	−7.0–6.9	−140.3
Trimethylethene	*Tert.*-amyl alcohol and oxalic acid	38.4–38.45	−134
Isopropylethene	Dehydration of iso-amyl alcohol over alumina and treatment of product with dilute sulfuric acid	20.1–20.4	.....

[a] All the samples were finally purified by fractionation in a vacuum-jacketed spiral column. For details of the preparations see Davis, THIS JOURNAL, 50, 2769 (1928); Ind. *Eng.* Chem., Anal. *Ed.*, 1, 61 (1929). For isopropylethene the method of Norris and Reuter was used, THIS JOURNAL, 49, 2526 (1927). The sample of trimethylethene was supplied by Mr. George Thomson.

[b] The freezing-point curves were kindly made by Professor E. L. Skau of Trinity College, Connecticut, who also supplied the following information drawn from the freezing-point curves. The isobutene is really quite pure. The 2-butene from 2-butanol and phosphoric acid seems to be a mixture. That from *sec.*-butyl iodide and alcoholic potash is better but is still far from pure. However, it may be noted that all the freezing points are higher than those found by Coffin and Maass for these substances: *iso*-butene, 146.8°; 2-butene, −127° [THIS JOURNAL, 50, 1433 (1928)]. The samples of 1-butene and *iso*propylethene did not freeze in liquid air (Coffin and Maass, supra, Norris and Reuter, ibid.).

TABLE VI

ABSORPTION RATES PER UNIT AREA ($C \times 10^4$) FOR ETHYLENE INTO CONCENTRATED SULFURIC ACID AT DIFFERENT RATES OF ROTATION AND FOR DIFFERENT VOLUMES OF ACID

Expt.	H_2SO_4, cc.	R.p.m., 0	R.p.m., 7	R.p.m., 38–44	R.p.m., 100	R.p.m., 200
3	10	1.97	1.72	2.02	2.48	2.00
2	30	1.90	1.78	2.33	3.12	..
4	90	1.62	1.44	2.02	..	3.93

These results show that for the absorption of ethylene into concentrated sulfuric acid: (a) the film of acid on the glass absorbed as well per unit area as the surface of the acid itself, (b) the absorption rate was not greatly changed by the renewal of the surfaces or by the agitation in the liquid caused by rotation.[4] (c) The rate was hardly affected by a nine-fold change in the volume of the acid. Accordingly it must be concluded that the reaction between the ethylene and sulfuric acid took place entirely in a very thin film at the surface. The ethylene never reached the main body of the acid at all.

Similar conclusions hold for the absorption of ethylene into 80% acid and of isobutene into 70% acid (see Table III). In other cases the values for C at r.p.m. = 0 are quite different from those obtained with the chamber rotating. These divergencies might in part be attributed to errors in the former measurements, e. g., part of the glass surface is wetted by acid drawn up through surface tension. They are worthy of further study because of their bearing on the selection of methods for separating olefins in gas analysis by selective absorption in sulfuric acid.[5]

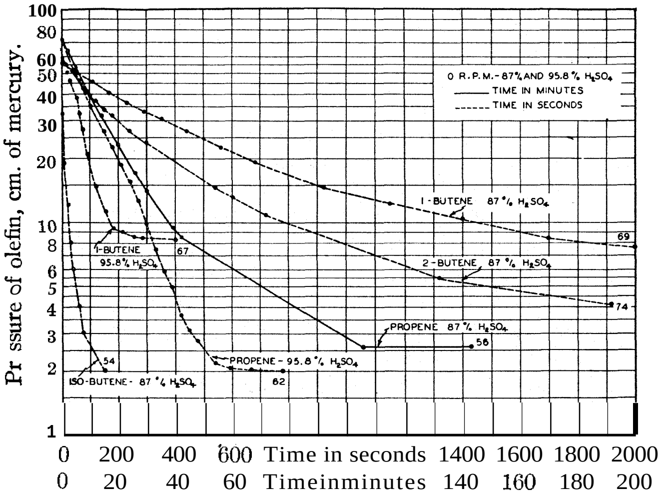

Fig. 3.

The Effect of Foreign Gases (Table II).—Propene was absorbed into 87% sulfuric acid from a 77% mixture with oxygen (No. 40) at the same rate, $C = 39.8$, as pure propene, $C = 38.2$. Nor was its absorption affected by the presence of an equal volume of ethylene (No. 41) $C = 39.9$. Tri-

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[4] This very important conclusion has since been confirmed by absorption measurements in another apparatus where the liquid can be stirred without changing the area of its surface. Identical rates of absorption for ethylene into concentrated sulfuric acid were found when the rates of stirring were, respectively, 0, 90 and 480 r.p.m. Full details will be published later. On the other hand, Becker, *Ind. Eng. Chem.*, 16, 1236 (1924), showed that slow stirring (60 r.p.m.) increased the rate of absorption of oxygen into water 25 times.

[5] Unpublished data by Davis and Quiggle show that propene is absorbed about 1000 times faster than ethylene by 87% sulfuric acid in an Orsat pipet. Compare the corresponding ratios in Table IV, 550 at r.p.m. = 0 and 362 at r.p.m. = 28.

methylethene vapor was absorbed at the same rate when pure and when mixed with 96% of air (Nos. 43 and 44).

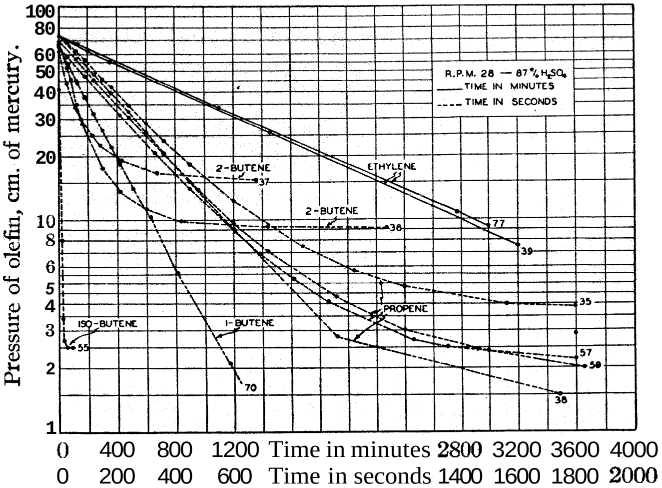

Fig. 4.

The Relation between the Acid Concentration and the Relative Rates of Absorption of Ethene and Propene (Table IV).—Considering only the measurements made on these two gases with the chamber rotating, those

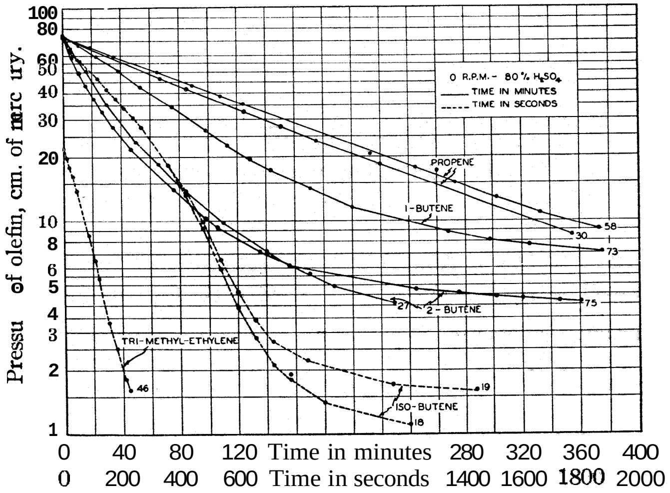

Fig. 5.

for 80 and 87% acid are the most reliable both because of the number of check experiments and because of the magnitudes of the pressure changes and of the periods of time involved. The values for propene in 95.8%

acid and for ethene in 60% acid are approximate only, because the former was a very rapid and the latter a very slow absorption.

It appears then that, within the accuracy of the measurements, the absorption rate of propene remained always about 300 times that of ethylene for concentrations of acid from 80% to concentrated, this in spite of the fact that the absolute values for the rates of both changed almost 200 times. This result is of importance in relation to the selection of the concentration of sulfuric acid most suitable for selectively absorbing propene from gases containing ethylene in the manufacture of *iso*propanol. It also raises doubt as to whether the superior merits claimed by Tropsch and Philippovich[6] for 87% acid in gas analysis absorptions for separating propene and its higher homologs from ethylene will hold for all types of pipets.

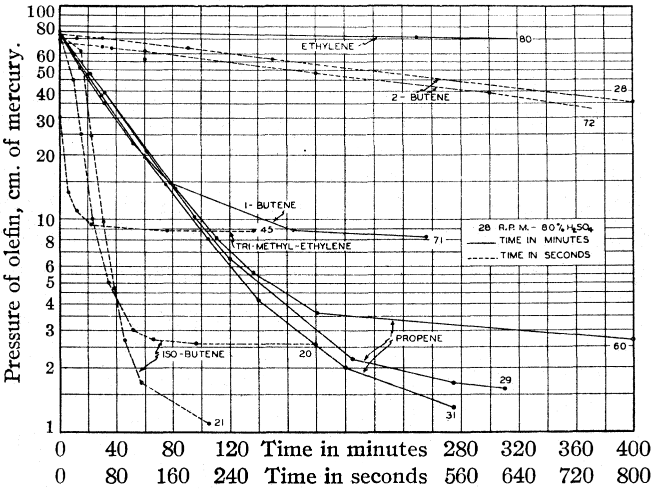

Fig. 6.

The Relative Rates of Absorption of Propene and the Three Butenes (Table IV).—The results show conclusively that propene and 1-butene

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[6] Tropsch and Philippovich, *Brennstoff-Chem.*, **4, 147 (1923).** It may be noted that the following table prepared from the excellent data of these observers on absorptions from synthetic mixtures of ethylene and propene hardly supports their conclusion.

H_2SO_4 used, %	**99**	**90**	**88**	**87**
Contact in Hempel pipet with pearls, minutes	5	2	5	5
Relation of absorption to propene taken, %	100	104, 99.7, 99.5	102, 92	96.1, 100

Manning, King and Sinnatt, *Dept. Sci., Ind. Research* (Brit.), Technical Paper No. **19,** p. **8,** who used **87%** acid for this purpose in a standing pipet, found it necessary to correct for the ethylene absorbed. They state "It is interesting to note that the diminution in volume after ten minutes' absorption does often coincide with the true volume of the higher olefins as found by the above method (T. and P.), the small ethylene absorption compensating at that moment for the residual unabsorbed higher olefins."

dissolve at about the same rate in sulfuric acid of any concentration. Indeed for dilute acids it is uncertain which dissolves the faster. This question has considerable theoretical importance and is being investigated further. The somewhat higher rate of 1-butene, relative to propene, in concentrated acid may be due to its greater ease of polymerization.

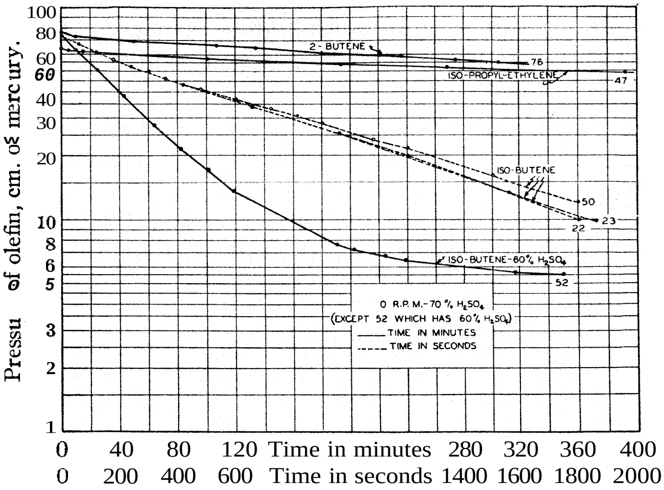

Fig. 7.

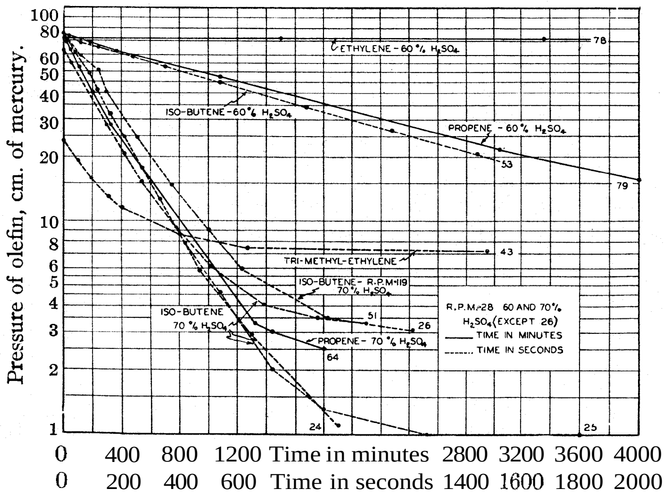

Fig. 8.

The ratio of the absorption rate of 2-butene to 1-butene is remarkably constant, 1.7 to 2.6 for 70 to 87% acid.

These facts show the unreliability of certain gas analysis methods which have been proposed involving the separation of the normal butenes from propene by selective absorption in sulfuric acid. This subject will be dealt with in another paper.

The values for isobutene vary in a puzzling manner However, it dissolved about 10 to 80 times as fast as 2-butene, which shows that it can be separated from propene and the normal butenes by selective absorption in sulfuric acid, although not as sharply as can propene from ethylene.

Isobutene and Trimethylethene (Table II).—According to our measurements, trimethylethene vapor was absorbed three to four times faster than gaseous isobutene into 80% sulfuric acid and 1.3 times faster into 70% acid. However Michael and Brunel[7] showed that when liquid

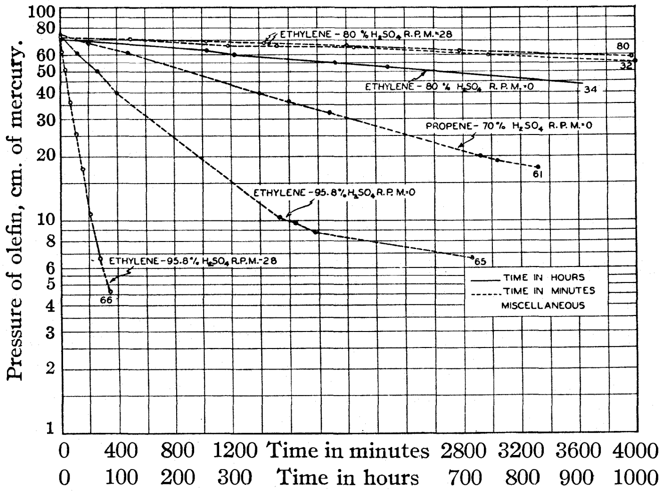

Fig. 9.

isobutene and trimethylene were shaken with 65% sulfuric acid or with more dilute acids in sealed tubes under similar conditions, isobutene dissolved at least three times as fast as trimethylethene.

Consideration must, however, be given to the differences in the conditions existing in the two methods of experimentation. In that of the writers the ratio of the absorption coefficients (C) of two olefins shows the ratio of the quantities which are dissolved when their gaseous partial pressures are equal. On the other hand, in the reaction tubes of Michael and Brunel the partial pressure of the isobutene (b. p. −6.8") must have been much larger than that of the trimethylethene (b. p. 38.4°).

From data obtained by the same experimental procedure, these investigators have compared relative rate of reaction with sulfuric acid for the two liquids cited above and also tetramethylethene (b. p. 71–72") and

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[7] Michael and Brunel, *Am. Chem. J.*, **41, 118** (1909)

di-isobutene (b. p. 102–102.5°). When two liquids dissolve in and react with a solvent, to what extent are their relative rates of solution, on shaking, characteristic of their rates of reaction in the solution?

Isopropylethene.—The two measurements Nos. 42 and 47 indicate that this olefin is absorbed only slowly by 70% sulfuric acid at a rate comparable with that of propene.

The Researches of Michael and **Brunel.**[7]—These investigators measured the rates at which the individual butenes were absorbed when shaken with sulfuric acid of various concentrations in Hempel pipets. It has been pointed out by one[8] of us from their data that approximately the same fraction of the olefin was dissolved in unit time over the whole range of each experiment. This is also clearly shown by the fact that the absorption curves when plotted on semi-logarithmic paper are nearly straight lines (Fig. 10).

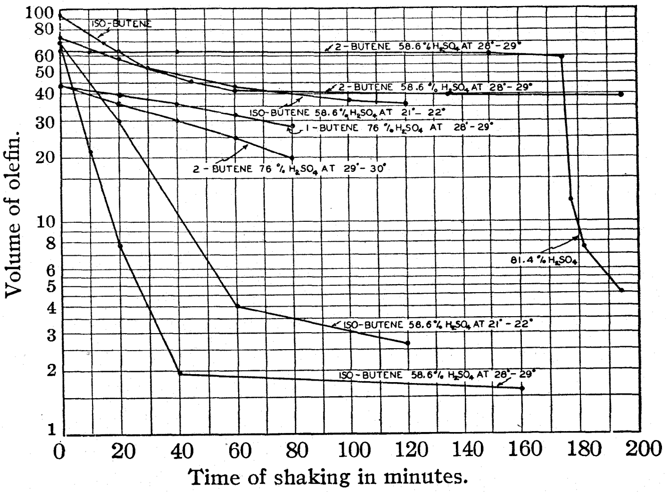

Fig. 10.—Michael and Brunel's absorptions in Hempel pipets.

This experimental fact could be explained if the amount of the absorption was always proportional to the area of the absorbing surface and if this area decreased proportionally with the gas volume. The actual relationships between the volumes of gas and the surfaces exposed in an ordinary Hempel pipet are shown in Table VII.

Michael and Brunel assumed that the rate of absorption of the olefin was proportional to the area of the liquid surface and corrected for variations in the sizes of their pipets on that basis. However, as has been shown above, a fresh acid film on the glass is as effective for absorption per unit area as the liquid surface itself, and moderate shaking wets the whole

[8] Davis, This JOURNAL, 50, 2780 (1928).

surface of a Hempel pipet if the gas volume is not excessive. As a first approximation the area of the absorbing surface may be taken as the sum of the liquid surface and of the glass above it with the pipet at rest. Table VII shows that this total area holds a more constant ratio to the gas volume than that of the liquid surface only.

TABLE VII

RELATIONS BETWEEN GAS VOLUMES AND ACID SURFACES FOR A SPHERICAL HEMPEL PIPET OF 175-CC. CAPACITY AT REST

r = radius. h = distance from center to liquid level

h cm.,	Volume of gas. cc. $\frac{2}{3}\pi r^3 - \pi\left(r^2h - \frac{h^3}{3}\right)$	Liquid surface sq. cm. $\pi(r^2 - h^2)$	Glass surface above liquid, sq. cm. $2\pi r(r - h)$	Total liquid and glass surface exposed, sq. cm.	Ratio of liquid surface/ vol of gas	Ratio of total surface/ vol. of gas
−1	124	35	97	132	0.28	1.16
0	88	38	76	114	.43	1.30
+0.5	69	37	65	102	.54	1.48
1	51	35	54	89	.68	1.74
1.5	34	31	43	74	.89	2.14
2	20	25	32	57	1 23	2.8
3	2.4	10	10	20	4 0	8 2

Nevertheless, for gas volumes from 70 to 20 cc. the ratio of the total surface to the volume changes about 100%, while some of the curves for the absorptions of Michael and Brunel remain fairly straight for even larger changes of gas volume. It appears that the course of their absorptions in Hempel pipets, moderately shaken, was much more uniform than would be predicted from the postulate that the quantity absorbed in unit time was always proportional to the total area of the liquid surface and the film on the glass measured at rest. This is not an academic problem. It is fundamental for the standardization of selective absorptions in gas analyses that the laws governing the absorption rates should be known for the various types of pipets.

To calculate the specific absorption coefficients C from the data of Michael and Brunel the constants $K = 1/t \ln (V_0/(V_0 - V_t))$ as calculated from the absorption curves, must be multiplied by the ratio of the volume of the gas to the area of the absorbing surface. Taking the ratio of total acid surface to volume existing for 50 cc. of gas, the following values were calculated in two cases where comparisons could be made with ours for the rotating absorber.

Absorption conditions	C
2-Butene into 81.4% H_2SO_4 in Hempel pipet at 28–29°.	55 X 10^{-4}
2-Butene into 80% H_2SO_4 in rotating absorber at 25°...	10.5 X 10^{-4}
Isobutene into 58.6% H_2SO_4 in Hempel pipet at 28–29°.	12 X 10^{-4}
Isobutene into 60% H_2SO_4 in rotating absorber at 25°...	9.7 X 10^{-4}

The agreement is rather remarkable. In the case of 2-butene they used a stronger acid at a higher temperature than we and a greater value for *C* would be expected. In the case of *iso*butene the effects of the differences in acid concentration and in temperature tended to counterbalance.

The Research of A. Dobrjanski.[9]—Instead of a Hempel pipet, this investigator used a glass cylinder of constant cross section for absorption into sulfuric acid. The olefin gas was introduced from a mercury buret, and in taking the separate volume readings as the absorption proceeded only part of the gas was withdrawn into the buret, apparently up to a fixed mark in the chamber. After a somewhat higher initial rate had subsided, each olefin gas dissolved at uniform speed for a long time. In each experiment an excess of acid 800 to 1000 times the theoretical was used.

Dobrjanski criticizes the use of Hempel pipets by Michael and Brunel for measuring absorption rates because, as pointed out above, the ratio of the area of the liqud surface to the volume of the gas changes as the absorption proceeds. For this reason he used a vessel of constant cross section 19.5 sq. cm. and tried to avoid wetting the upper surfaces during the volume readings. Unfortunately he does not seem to have recognized the high absorbing capacity of the acid films left on the glass and the errors from this source appear to have vitiated much of his otherwise valuable data.

He attributes the high initial rates of absorption to physcal solution of the gases in the acid. It seems more probable, however, that the observed effect was due to absorption into the film of acid left on the whole glass surface when the acid was forced down to admit the gas at the beginning.

For ethylene and propene the absorptions were carried out in three ways: first with the pipet at rest, second with the acid in the pipet tossed back and forth every five minutes, which about doubled the rate, and third with the pipet shaken continuously 120 times per minute, which increased the rate 5 to 28 times, depending on the concentration of the acid. The volume readings were taken every ten minutes. Evidently such procedures will give great variations in the total area of the absorbing surface and in the freshness of the acid film. It is not possible to calculate from Dobrjanski's data specific absorption coefficients comparable to ours and even his values for the relative rates of absorption of the different olefins appear to be only qualitative.

The present paper deals only with experimental investigations of the rates at which olefins are absorbed by sulfuric acid. The expression "rate of reaction" has been purposely avoided. The relationships between the rates of absorption of gases and the rates and types of the reactions which take place in solution need further consideration. The magnitudes of the physical solubilities of the gases and their rates of diffusion in the

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[9] Dobrjanski, *Neftyanoe Khozyaistvo,* 565–737 *(1925).* For a critical translation of this article we are indebted to Professor Paul N. Kogerman.

solution are important factors. Nor should the possibility be overlooked that reactions may take place between the gaseous olefin molecules and the surface molecules of the acid.

Summary

1. Measurements have been carried out on the rates of absorption of olefin gases and vapors into sulfuric acid at constant volume by following the change in the gaseous pressure with time.

2. The logarithms of the olefin pressures plotted against periods of absorption form fairly straight lines. That is, the quantity absorbed in unit time was proportional to the partial pressure of the olefin.

3. When the reaction tube was rotated, the increase in the total absorption was largely proportional to additional area of acid surface formed on the glass.

4. Specific absorption factors (C) have been calculated on all the gaseous olefins into a large excess of sulfuric acid of various concentrations at 25° (Table III). They represent the cc. of gas absorbed, at constant pressure, by 1 sq. cm. of acid surface in one second and appear to be definite entities. They were often unaffected by the rate of renewal of the acid surface, by variations in the volume of the acid or in the degree of its agitation.

5. The reactions appeared to take place in a very thin film at the surface of the sulfuric acid. The gases never reached the main body of the liquid. Accordingly it seems advisable to use caution in drawing conclusions regarding the rates of reaction of gases with liquids in which they are sparingly soluble, from their rates of absorption.

6. Objections are raised to the practice of drawing conclusions regarding the relative rates of reaction of two liquids with another liquid from measurements of their relative rates of solution in it on shaking.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION PROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 50]

STUDIES IN AUTO-OXIDATION REACTIONS. I. OXIDATION OF ANETHOL, ETC.[1]

BY NICHOLAS A. MILAS[2]

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Introduction

In a very recent article[3] the author presented some evidence to show that "true" auto-oxidation reactions[4] are not only susceptible to inhibitory and accelerating action of small quantities of certain types of inorganic as well as organic substances, but are also capable of inducing the oxidation of other substances which ordinarily are not easily oxidized with molecular oxygen. Purthermore, it has been shown by Moureu and his collaborators[K] and more recently by the author[6] that auto-oxidation reactions induce the polymerization of unsaturated substances such as acrolein, styrene, iso-eugenol, etc.

Still another important characteristic which seems to be capable of generalization is the occurrence of a maximum oxygen absorption rate in all typical auto-oxidation reactions. The significance of this maximum rate was recently emphasized by the author,[7] who pointed out the existence of a definite'quantitative relationship connecting these maxima and the concentration of certain inhibitors such as anthraquinone and benzoquinone.

As a result of the tremendous interest shown recently in auto-oxidation reactions by various investigators, several methods have been developed for the measurement of oxygen absorption rates. Moureu and his coworkers: who carried out the principal part of the work in this field, employed a method which seems, in the opinion of the present author, to be inadequate for accurate quantitative measurements due to a failure of the investigators to observe the following facts.

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[1] Some of the preliminary experiments were carried out at Princeton University while the author was serving as a National Research Fellow in Chemistry (1926–1928).

[2] Research Associate, Massachusetts Institute of Technology.

[3] Milas, J. *Phys. Chem.*, 33, 1204 (1929).

[4] Oxidation reactions in which molecular oxygen adds to the substance to be oxidized to form a dative peroxide, rather than dehydrogenation reactions as postulated by Wieland *[Ber.,* 45, 484, 679, 685, 2603 (1912), and subsequent articles up to and including (1929)].

[5] Moureu and Dufraisse, *Bull. soc. chim.*, 31, 1152 (1922); 35, 1564 (1924); Moureu, Dufraisse and Badoche, *ibid.*, 35, 1591 (1924).

[6] Milas, *Proc. Nat. Acad. Sci., 14,* 844 (1928).

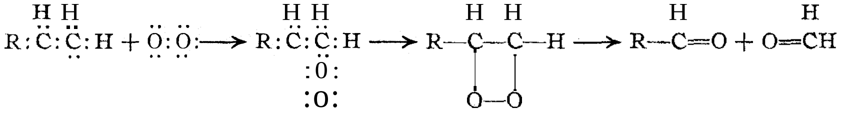
[7] Milas, *ibid.*, 15, 596 (1929); *cf.* Brunner, *Helv. Chim. Acta, 10,* 707 (1927).

[8] Moureu and Dufraisse, *Chem. Rev.*, 3, 113 (1927); J. *Soc. Chem. Ind., 47,* 819, 848 (1928).

1. Considerable changes in pressure during oxidation with oxygen are known to influence greatly the rates of oxygen absorption. This fact has been more clearly demonstrated recently by Chariton and Walta[9] and by Semenoff[10] in the case of the slow oxidation of phosphorus.

2. Oxidation of organic liquid substances with oxygen constitutes a two-phase system, and to determine the reaction rate between the two phases, the conditions must be such that the two phases are constantly at equilibrium with each other. In other words, the liquid must be always saturated with oxygen during the course of the reaction.[11] Furthermore, there seems to exist a tendency, in highly polymerized liquids, for the formation of a surface film consisting chiefly of polymerized molecules which increase the viscosity of the surface layer and consequently diminish the diffusion rate of oxygen. Rapid stirring or shaking of the reaction mixture will therefore prevent the formation of such a film.

3. In auto-oxidations of substances such as styrene, anethol and the like, the peroxides formed are extremely unstable even at room temperatures and are known to break down to form two aldehyde molecules. Following the scheme previously suggested by the author,[3] the oxidation may be expressed in general in the following manner



$$R:\overset{H}{\ddot{\underset{..}{C}}}:\overset{H}{\ddot{\underset{..}{C}}}:H + \ddot{\underset{..}{O}}:\ddot{\underset{..}{O}}: \longrightarrow R:\overset{H}{\ddot{C}}:\overset{H}{\ddot{\underset{\substack{:\ddot{O}:\\:O:}}{C}}}:H \longrightarrow R-\underset{|}{\overset{H}{C}}-\underset{|}{\overset{H}{C}}-H \longrightarrow R-\overset{H}{C}=O + O=\overset{H}{C}H$$

In a closed static system, similar to that used by Moureu and his co-workers,* the gaseous aldehydes formed during the reaction seem to have, as it will be shown presently, a decided inhibitory effect on the rate of the reaction, since an intermittent removal of these aldehydes increases considerably the rate of oxygen absorption. The inhibitory action of the gaseous aldehydes is presumably both physical and chemical in nature. The evolution of gases in a closed system would surely increase the pressure of the system and the resulting effect would be equivalent to an apparent decrease in the oxygen absorption rate. Then, too, the inhibitory action of these aldehydes might conceivably be due to the fact that they are partly oxidized inducedly to the corresponding acids. These acids have been actually isolated in the majority of the cases studied by the author. A third possibility, which should not be overlooked, is that of a compound formation between the gaseous aldehyde and the original ethylenic substance. That an unstable intermediate complex formed in this manner decreases the oxygen absorption rate has been demon-

[9] Chariton and Walta, Z. *Physik,* 39, 547 (1926).

[10] Semenoff, *ibid.,* 46, 109 (1927).

[11] Reinders and Vles, *Rec. trav. chim.,* 44, 1 (1925); Reiff, THIS JOURNAL, 48, 2895 (1926); Alyea and Bäckström, *ibid*, 51, 94 (1929).

strated recently by the author.' Moreover, Prins[12] has actually shown that styrene, anethol, etc., do condense, under the influence of certain reagents, with formaldehyde to form definite compounds.

The present investigation, therefore, gives a general outline of the method adopted for the accurate measurement of oxygen absorption rates and some of the reactions studied.

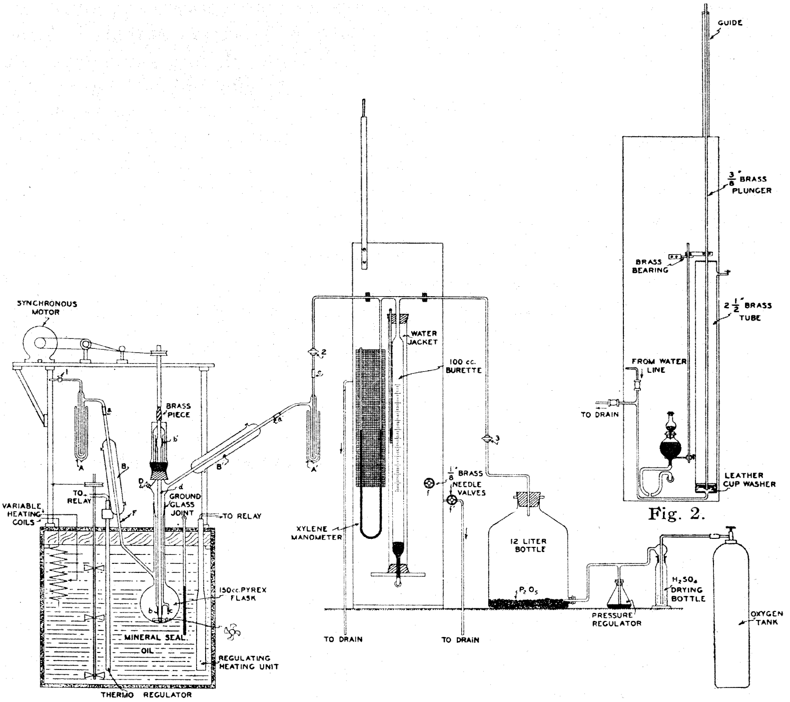


Fig. 2.

Fig. 1.——Apparatus for oxygen absorption measurements.

Fig. 2. (Above)—Hydraulic mercury lifting device.

Experimental Part

Apparatus and Method of Measurements.—A complete description of the apparatus as finally adopted is shown in Figs. 1 and 2. The reaction apparatus consists of a 150-cc pyrex bulb connected by means of a ground joint to a mercury seal. The reaction mixtures are stirred by an efficient glass stirrer sealed onto the lower end of the glass tube *d* which is prevented from wobbling by the glass bearings *b* and *b'*. The nozzle *c* allows both the liquid to be oxidized and the oxygen to pass freely down into the bulb. The gases which are formed during the reaction are constantly driven away from this nozzle by the centrifugal whirling motion of the stirrer, thus allowing the oxygen which passes down through it to come into a more intimate contact with the liquid. This entire portion of the apparatus is connected by two small pieces of pressure rubber tubing *a* and a' to traps *A* and *A'*, both of which are immersed in a mixture of ether–carbon

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[12] Prins, *Proc. Acad. Sci. Amsterdam,* **22,** 51 (1919); *Chem. Weekblad,* 16, *1072* (1919).

dioxide ice. The trap *A'* serves to catch any impurities such as water and xylene vapors, etc.. that may be easily found in the apparatus to the right of stopcock No. **2.** Trap **A,** on the other hand, serves to condense the volatile gases, which can then be identified and estimated quantitatively at the end of each reaction.

The hydraulic mercury lifting device shown in Fig. **2** (back view of board in Fig. 1) constitutes a decided improvement to the original apparatus constructed by the author at Princeton University. It has rendered laborious and rapid measurements more easy and more accurate. This device is a modification of that reported by Tauch[13] and has been designed to operate at water pressures as low as 6 lb. per square inch.[14] The operation of this device is so adjusted that when the bottom of the brass plunger reaches the overflow pipe, it stops automatically and the mercury level of the bulb coincides exactly with the zero mark of the buret. Then, again, when the plunger is at the bottom of the brass tube, the mercury level coincides with the 100th mark of the buret. The device is operated by the two needle valves f and f'. When *f'* is closed and f is entirely open, it requires from forty-five to fifty seconds to fill the buret with mercury, while the reverse process can be accomplished in thirty to thirty-five seconds. This speed was never attained in actual oxygen absorption measurements.

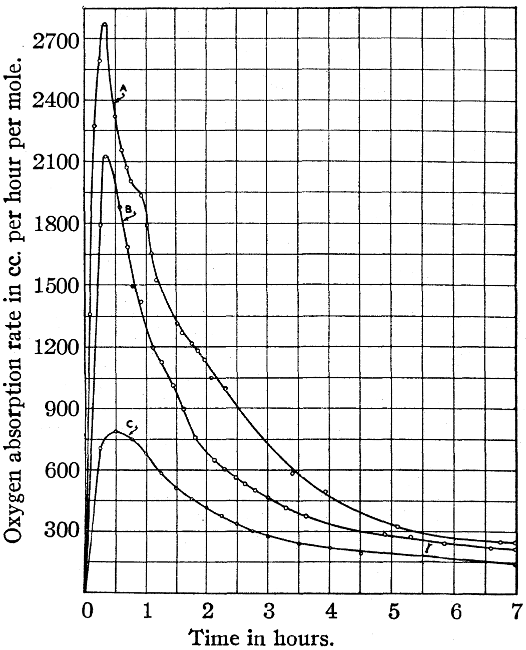

Fig. 3.—Oxidation of iso-eugenol.

The temperature at which the measurements were carried out was 110 ± 0.1°, and the reaction mixtures were stirred at the rate of 1200 ± 15 r.p.m. with the exception of the experiments with iso-eugenol and iso-safrole, in which the rate of stirring was 700 ± 15 r.p.m. The revolutions were measured by a revolution counter accurate to ±2 r.p.m.

Before each experiment the reaction apparatus was cleaned as follows: washed with hot soap solution, then with water, then filled with freshly made cleaning solution and allowed to stand for some hours. The cleaning solution was then poured out and the apparatus washed once with pure concentrated nitric acid, followed by a thorough rinsing with water and then with distilled water. It was next rinsed twice with 95% alcohol and finally twice with anhydrous c. p. ether free from peroxides. The entire apparatus was then heated while dry air was allowed to pass through it in a hot-air oven kept at about 120°. This treatment of the apparatus insured very consistent results. After the above treatment, the apparatus was connected as shown in Fig. 1 and oxygen was allowed to pass through it slowly for at least one hour.

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[13] Tauch, Ind. Eng. Chem., 19,1349 (1927).

[14] The author wishes to acknowledge advice received from Professor J. J. Eames of the Mechanical Engineering Department in the designing of this device.

Just before the addition of the substance to be oxidized, the apparatus was tested for leaks by closing stopcocks I and **3,** keeping 2 open and increasing or decreasing the pressure in the system from 20 to 30 mm. of xylene. If the xylene levels remained the same for at least thirty minutes, the apparatus was ready for the experiment. Stopcock **3** was then opened, the ground-glass stopper D removed and the liquid to be oxidized dropped into the apparatus by means of a special calibrated pipet. Stopper D was then quickly replaced and stopcock **3** again closed. It may be remarked here that the whirling motion of the rotating tube *d* not only carries the liquid rapidly into the bulb but causes it to become quite readily saturated with oxygen. During the first one or two minutes the pressure in the apparatus increases, due to the heating and expansion of the added liquid, then becomes constant and finally begins to decrease. The time at which the pressure has become constant is taken as the zero time of the reaction. During the oxygen absorption measurements the pressure within the system was kept constant to within **1** to 2 mm. of xylene. In experiments in which the oxidizing liquid had a very high boiling point, the water condenser B was omitted.

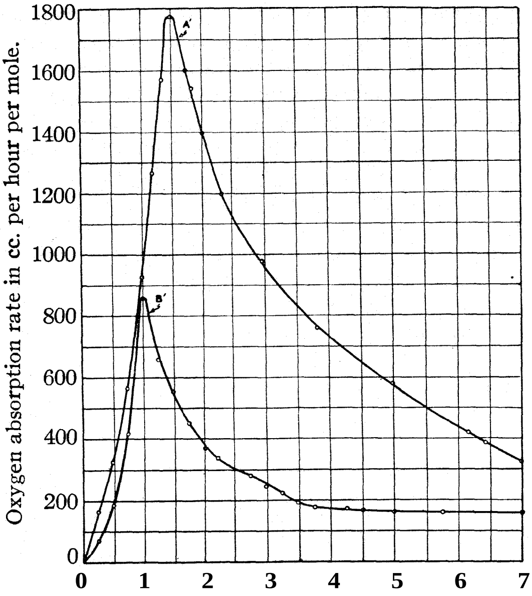

Fig. 4.—Oxidation of iso-safrole.

The **Intermittent** Method.—All oxygen absorption measurements, with the exception of a few with iso-eugenol and iso-safrole, were determined by this method. The method consists in making measurements for a definite interval of time, then allowing the oxygen to sweep through the apparatus, also for a definite interval of time, at a definite rate, usually 1 to **2** bubbles per second. This process is repeated throughout the experiment. On sweeping through the apparatus, the oxygen removes practically all the gaseous aldehydes soon after their formation, thus increasing the oxygen absorption rate in accordance with criterion **(3)** as set forth in our introduction. Measurements on iso-eugenol and iso-safrole[15] shown by Curves **A,** B, C and A', B', respectively, of Figs. **3** and 4 clearly substantiate our contention. All the experiments represented by these curves have been repeated and verified. In Expts. C and B' a closed system was employed with the entire branch *F* of the apparatus omitted. The reaction mixtures were stirred at *700* ±15 r.p.m., and the measurements were made at constant pressure as before. No oxygen was passed through the apparatus. All experimental values for oxygen absorption rates have been calculated to N. T. P. Similar measurements were carried out for experiments B and **A',** except that the apparatus used was as represented by Fig. 1[15] with stopcock 1 closed during the entire period of the experiments. Curve **A,** on the other hand, represents the results obtained when the intermittent method was

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[15] These experiments were carried out in the fall of 1927 using the original form of the apparatus without the hydraulic lifting device.

employed. Moreover, the identification and quantitative estimation of the products formed in each case fully corroborate the oxygen absorption measurements. From Expts. *C* and B' only minute quantities of vanillin and piperonal were detected. (The reagents used for the detection and estimation of these aldehydes were *p*-nitrophenylhydrazine[16] in acetic acid and semicarbazide in sodium acetate solution.) Experiments A and A', on the other hand, yielded *inter alia* 21% vanillin and 17% piperonal, respectively, for runs of the same number of hours (30).[17]

Materials Used

Iso-eugenol.—Iso-eugenol (Eastman Kodak Company, c. p. quality) was vigorously shaken with a 35% solution of sodium bisulfite, washed with water and dried over anhydrous sodium sulfate. It was then fractionated under diminished pressure in a stream of nitrogen which was first bubbled through a strong solution of pyrogallol in caustic soda, then through concd. sulfuric acid and finally passed through asbestos wool. The fraction boiling at 109–110° (2.5 mm.) was collected and kept in a brown bottle under pure nitrogen.

Iso-safrole.—Iso-safrole (Eastman Kodak Company practical grade) was first washed with dilute sodium hydroxide solution, then treated further as was iso-eugenol. When fractionated in a stream of pure nitrogen, the fraction boiling at 90–92° (*2* mm.) was collected and kept in a brown bottle under pure nitrogen. As the experiments with iso-safrole and iso-eugenol constitute some of the early experiments carried out by the author, no special precautions were taken similar to those described with anethol. Twenty-g. samples were directly weighed in small Erlenmeyer flasks and then transferred to the main apparatus.

Anethol.—Anethol, like styrene,[6] is extremely sensitive to light and atmospheric oxygen. Special precautions were, therefore, necessary not only for its purification but also for its storage. The c. p. product furnished by the Eastman Kodak Company was treated following the method used with iso-safrole, then fractionated twice under diminished pressure in a stream of pure nitrogen. The second fractionation was carried out in a dark room using only a small red light to watch the thermometer. The fraction boiling at 79.5–80.5° (2 mm.) was collected directly in a brown bottle like that shown in Fig. 5 and kept under pure nitrogen. To avoid any oxygen entering the bottle during the withdrawal of samples by means of a special pipet, nitrogen was allowed to pass through from left to right with clamps e opened and *e'* closed. Immediately after the removal of the pipet, the cross-like tube is tightly stoppered, clamp *e* closed and *e'* opened and the bottle evacuated. Pure nitrogen is then allowed to fill the bottle and clamps e and *e'* are tightly closed. This method of purification and storage of anethol was found to give very satisfactory results.

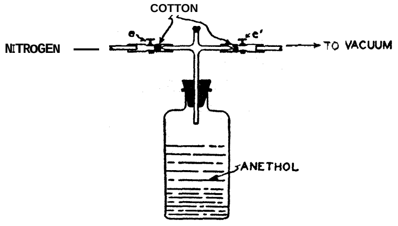

Fig. 5.

Anisaldehyde.—Anisaldehyde (Kahlbaum) was further purified by precipitating it as the sodium bisulfite addition product, which was subsequently decomposed with a 10% solution of sodium carbonate. The aldehyde was separated, washed with water and dried over anhydrous sodium sulfate. It was fractionally distilled in a dark room

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[16] Bamberger and Sternitski, *Ber.*, 26, 1306 (1893); Parry, "The Chemistry of Essential Oils" (4th ed.), Scott, Greenwood and Son, London, 1922, Vol. II, p. 343.

[17] These experiments and several others with eugenol and safrole will be reported in detail elsewhere.

under diminished pressure in a stream of nitrogen, and the fraction boiling at 86.5–87.5° (2 mm.) collected and kept in a brown bottle similar to that shown in Fig. 6.

Benzoperacid.—Benzoperacid was prepared following the modified method[18] of Raeyer and Villiger.[19] This acid was obtained in the solid state having an activity of 94% when used. It was found best to add the benzoperacid to the anethol in an atmosphere of nitrogen and then add the entire mixture to the main apparatus.

Anthracene.—The anthracene used was the C. P. grade (a qualitative test showed the absence of anthraquinone) furnished by the Eastman Kodak Company. Anthracene, as well as all the other inhibitors except anisaldehyde and benzoquinone, was added to the apparatus previous to the addition of anethol to test its reactivity with free oxygen. None was found to absorb oxygen under the conditions of our experiment.

Anthraquinone.—Anthraquinone (Kahlbaurn's purest grade) was used without further purification.

Phenanthrene.—Phenanthrene (Kahlbaum) was recrystallized twice from 95% ethyl alcohol and dried-in a vacuum desiccator over concd. sulfuric acid; m. p. 100.3".

Phenanthrenequinone.—This substance was prepared by the oxidation of pure phenanthrene with chromic acid. It was recrystallized from 95% alcohol; m. p. 206°

Hydroquinone.—Hydroquinone (Eastman Kodak Company, C. P. grade) was used without further purification.

Benzoquinone.—Benzoquinone was prepared by the oxidation of pure hydroquinone with chromic acid. It was recrystallized twice from benzene and finally sublimed. Only the purest crystals of the sublimed quinone were used in the reactions studied. Since benzoquinone was found to sublime considerably at 110°, it was necessary to dissolve it first in anethol (this was done in a special apparatus filled with pure nitrogen), then the mixture was added to the main apparatus.

Carbazole.—Carbazole (Eastman Kodak Company, C. P. grade) was used without further purification.

Experiments with **Anethol.**—In all measurements of oxygen absorption rates it is of utmost importance that the results be reproducible and consistent to within a reasonable experimental error if they are to be employed for deductions of fundamental generalizations. Table I, therefore, shows the measurements of two typical experiments carried out one week apart. Measurements made from the same preparation of anethol at an interval of three months gave consistent results to within 2% of those shown in Table I. The results of Expt. 1 are also represented by Curve 1 of Fig. 6. The anethol was added to the apparatus, with all due precautions, by means of a special pipet, the air of which was replaced just before use by pure nitrogen. It was calibrated to deliver 19.851 g. of anethol. All experiments with anethol were run for a period of twenty hours each. During the time when measurements were not made, oxygen was allowed to pass slowly through the apparatus at the rate of about one to two bubbles per second.

Selective Inhibition and Induced Oxidation.—In a previous paper[6] the author has pointed out, for the first time, the existence of a selective inhibitory effect of anthracene during the oxidation of styrene. Anthra-

[18] Hibbert and Burt, THIS JOURNAL, 47, 2240 (1925).

[19] Baeyer and Villiger, *Ber.*, **33**, 1575 (1900).

TABLE I

OXYGEN ABSORPTION RATE OF ANETHOL

Total time, min.	0%-Absorption in cc./min.		0%-Absorptionin cc./min. corr. to N. T. P.		Oz-Absorption in cc./mole/min.		02-Absorption rate cc./mole/hr.	
	Expt. 1	Expt. 2	Expt. 1	Expt. 2	Expt. 1	Expt. 2	Expt. 1	Expt. 2
0	0	0	0	0	0	0	0	0
3	2.40	2.50	2.10	2.30	15.63	17.16	948	1,030
5	3.70	4.00	3.42	3.68	25.52	27.46	1,531	1,647
11	25.00	24.83	23.13	23.00	172.43	170.46	10,346	10,228
16	33.75	35.00	31.25	32.20	232.80	240.25	13,968	14,415
21	32.25	33.00	29.85	30.25	222.50	225.50	13,350	13,530
26	31.00	32.50	28.70	29.50	213.80	220.00	12,824	13,200
31	29.75	30.00	27.50	27.60	205.00	206.00	12,312	12,354
37	28.33	28.33	26.20	26.10	195.43	194.50	11,726	11,670
43	26.00	26.16	24.06	24.10	179.33	179.60	10,760	10,776
49	24.16	25.00	22.36	23.00	166.70	171.60	10,002	10,296
55	23.00	23.33	21.26	21.50	158.66	160.00	9,520	9,600
61	22.66	22.66	20.96	20.86	156.33	155.60	9,380	9,336
67	21.80	22.16	20.16	20.40	150.33	152.16	9,022	9,130
74	21.25	21.12	19.65	19.45	146.57	145.00	8,794	8,700
81	18.87	19.25	17.47	17.72	130.20	132.10	7,812	7,927
88	16.75	16.75	15.50	15.42	115.50	115.00	6,930	6,900
95	13.25	13.50	12.25	12.42	91.40	92.65	5,484	5,559

cene was found to inhibit the oxidation of benzaldehyde formed during the oxidation of styrene, but allow the oxidation of the latter to proceed at a relatively high rate. It was found, for example, that the maximum oxygen absorption rate of styrene was within 3.4% equal to the sum of the maximum oxygen absorption rates of pure benzaldehyde and styrene + anthracene. This relationship seems to hold also with anethol within 1.7%, as shown by the results of Table II. Curves 2 and 3 of Fig. 6 represent the oxygen absorption rates of anethol + anthracene and those of anisaldehyde, respectively, as plotted against time.

TABLE II

A COMPARISON OF MAXIMUM OXYGEN ABSORPTION RATES OF ANETHOL, ANETHOL + ANTHRACENE AND OP ANISALDEHYDE

Substance	Maximum O_2-absorption rate in cc./mole/hr.
Anethol	14,191
Anethol + Anthracene	9,860
Anisaldehyde	4,096
[Anisaldehyde + (Anethol + Anthracene)]	13,956

Method of Separation of Oxidation Products.—The following method has been adopted after trials with other methods including that of vacuum fractionation. At the end of each experiment the apparatus was disconnected and the volume of the condensed liquid in the trap tube A measured in a tube graduated to tenths of a cc. Although most of this liquid consisted of acetaldehyde, it also contained small amounts of paraldehyde[20] and acetic acid, the latter of which was directly titrated against standard sodium hydroxide solution. Minute traces of a high-boiling liquid, which was not identified, were also isolated.

The deeply brown and highly viscous reaction mixture was dissolved while still warm in 100 cc. of pure benzene and the solution shaken vigorously with 100 cc. of a 10% solution of sodium carbonate. This treatment removed the anisic acid and small quantities of acetic acid, both of which were recovered by acidifying this solution with sulfuric acid.[21] The benzene layer was then vigorously shaken with 35% solution of sodium

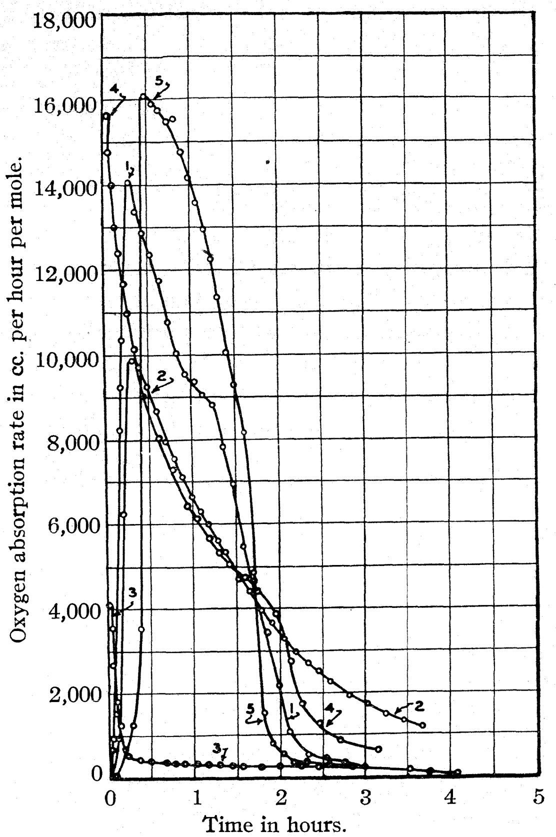

Fig. 6.—Oxidation and selective inhibition of anethol. Curve 1, 19.851 g. of anethol; Curve 2, 19.851 g. of anethol + 2.388 g. of anthracene; Curve 3, 22.237 g. of anisaldehyde; Curve 4, 19.851 g. of anethol + 0.6 g. of benzoperacid; Curve 5, 19.851 g. of anethol + 1.824 g. of anisaldehyde.

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[20] In the case of styrene oxidations, a solid polymer of formaldehyde was isolated.

[21] For estimation of acetic acid see Milas, This journal, 50,495 (1928)

bisulfite (at 60°) and allowed to stand overnight. This treatment removed anisaldehyde as the sulfite addition product, which was separated and determined as such. The benzene layer, after this separation, contained mostly polymers of anethol. However, when anthracene was used as the inhibitor, the benzene layer contained not only anethol but also anthracene and anthraquinone. To separate anthraquinone from the other substances the following method was developed. In certain cases in which anthraquinone was present in larger quantities than would dissolve in the volume of the solvent used, the undissolved portion was separated by filtration. The benzene layer was dried over anhydrous sodium sulfate, lots of 25 cc. were heated on the water-bath to remove the benzene and the residues treated with concd. sulfuric acid and heated further for half an hour. The entire mixture was then slowly poured into 200 cc. of boiling water, in which only anthraquinone precipitated out. This method is quantitative, as is shown elsewhere.' An alternative method based on the reduction of anthraquinonk to anthranol by zinc dust and caustic soda was also used to check the sulfuric acid method. An approximately quantitative estimation of the principal oxidation products of Reactions 1 and 2 is, therefore, given in Table III. The values given represent averages of duplicate runs of each reaction.

TABLE III

OXIDATION PRODUCTS OF REACTIONS 1 AND 2, REACTION TIME, TWENTY HOURS[22]

Substance	Reaction 1 anethol	Reaction 2 anethol + anthracene
Anisaldehyde	1.85%	14.5%
Anisic acid	13.8 %	2.3%
Anthraquinone	....	48.4%
Acetaldehyde	1.2 cc.	1.6 cc.
Acetic acid	0.12 g.	0.1 g.

It is sufficiently evident, therefore, from the foregoing results that anthracene inhibits the oxidation of anisaldehyde but allows the oxidation of anethol to proceed at a relatively high rate. For example, after four hours the oxidation rate of anethol had dropped down to less than 50 cc. per hour per mole, while that of anethol + anthracene was still 1160 cc. per hour per mole.

Curve 4 of Fig. 6 illustrates the effect of small quantities of benzoperacid on the rate of oxygen absorption of anethol during the initial stages of its oxidation. The positive catalytic effect of benzoperacid has been attributed to an increase of reaction chains by the energy liberated during the reaction of this acid with auto-oxidant molecules.[6,23]

Curve 6 of the same figure shows the effect of pure anisaldehyde on the rate of oxygen absorption of anethol. At a first glance of the maximum

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[22] Results reported elsewhere, Ref. *6*, p. 849, are for forty-eight hour runs.

[23] Backstrom, *Medd. Vet.-Akad. Nobelinst.*, **6,** No. **15** (1927).

value of this rate, one would conclude that anisaldehyde is a positive catalyst, whereas it actually shows an inhibitory action if one takes into consideration the time necessary for the rate to reach this maximum. The only available quantitative method, at present, which can be used to compare the inhibitory power of these inhibitors is that proposed recently by the author.[7] It has been shown that there seems to exist a definite relationship between the maximum oxygen absorption rate (V_m), the concentration of the inhibitor (C) and the time (t) necessary for V to reach the value V_m. These three variables seem to be related by the following empirical expression

$$V_m = K\frac{t}{C^{1/2}} \quad \text{or} \quad \frac{V_m C^{1/2}}{t} = K \qquad (1)$$

It may be mentioned here that the full physical significance of the square root of the concentration of the inhibitor is not completely understood in several cases. Column 5 of Table IV shows the values of K for the different inhibitors used as calculated from the above expression.

TABLE IV

INHIBITORY CONSTANTS OF VARIOUS INHIBITORS OF THE OXIDATION OF ANETHOL

Inhibitor	V_m In liters/hr./mole	C In moles/mole of anethol	t In min.	$\frac{V_m C^{1/2}}{t}$ or K
Hydroquinone	12.100	0.004998	388	0.0023
Benzoquinone	9.624	.004998	169	.0038
Anthracene	9.860	.099980	17	.1834
Anthraquinone	6.038	.099980	90	.0212
Phenanthrene	15.178	.099980	8	.6000
Phenanthrenequinone	4.952	.099980	30	.0522
Carbazole	8.408	.099980	74	.0359
Anisaldehyde	16.272	.099980	28	.1838

It may now be seen that the effect produced by anisaldehyde on the oxidation of anethol is almost identical with that produced by the same concentration of anthracene. Furthermore, the inhibitory power of the inhibitor seems to be an inverse function of the inhibitory constant. In other words, an inhibitor of very small inhibitory constant would have a very large inhibitory power and *vice versa*. Figure 7 shows the curves obtained when all the oxygen absorption measurements (except those of carbazole) have been plotted as before. From these curves it may be seen that phenanthrene (Curve 4), unlike the other substances, cannot be considered as an inhibitor of the oxidation of anethol. It is rather an accelerator, in spite of the fact that it is inducedly oxidized first to phenanthrenequinone and then to diphenic acid.

Discussion and Conclusions

In the experiments with anethol, iso-eugenol and iso-safrole, in the absence of inhibitors, there is an abnormal decrease in oxygen absorption rate long before an appreciable amount of the substance in question has undergone oxidation. These results would immediately lead one to suspect that such reactions are auto-inhibited and the inhibitor might be formed during their progress. If this view were correct, the addition of small quantities of different inhibitors such as anthracene, anthraquinone and phenanthrenequinone should cause the oxidation rate to fall off, after it had reached a maximum, considerably faster than in the case of pure anethol. Then, too, when an accelerator, such as benzoperacid, is added, the oxidation rate should fall off at a lower rate. However, the opposite is true in both cases, and in the case of inhibition the total amount of anethol oxidized for a definite period of time exceeds always the amount oxidized in the absence of inhibitors. The greatest amount oxidized in a twenty-hour period was that in Reaction 5 of Fig. 7 with phenanthrenequinone as the inhibitor. This reaction yielded 18% anisic acid and 29% anisaldehyde.

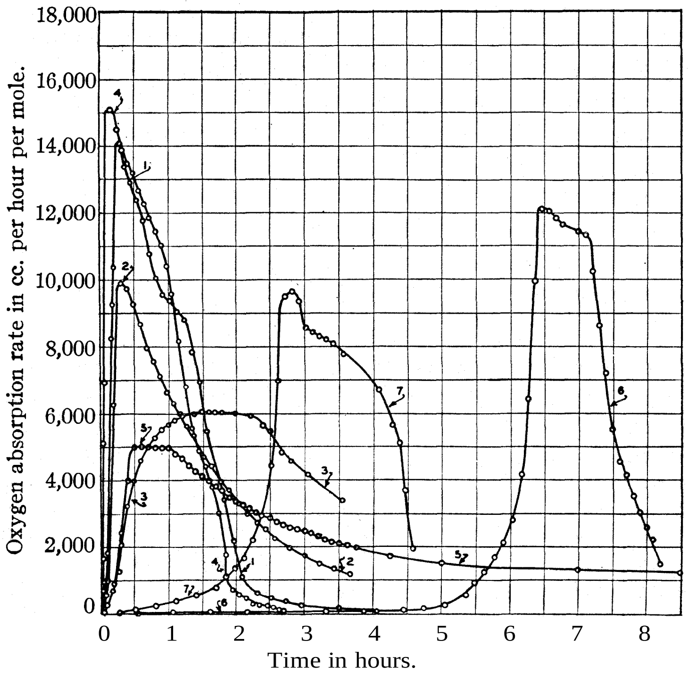

Fig. 7.—Effect of inhibition on oxygen absorption rate of anethol. Curve 1, 19.851 g. of anethol; Curve 2, 19.851 g. of anethol + 2.388 g. of anthracene; Curve 3, 19.851 g. of anethol + 2.790 g. of anthraquinone; Curve 4, 19.851 g. of anethol + 2.385 g. of phenanthrene; Curve 5, 19.851 g. of anethol + 2.790 g. of phenanthrenequinone; Curve 6, 19.851 g. of anethol + 0.0738 g. of hydroquinone; Curve 7, 19.851 g. of anethol + 0.0724 g. of benzoquinone.

What, then, constitutes a plausible explanation of these facts? In the oxidation of anethol and of other related substances, two main reactions should be considered: the reaction between active molecules of anethol and oxygen and that between active anethol molecules themselves to form polymers which no longer react with oxygen. The rate with which these two reactions proceed depends largely upon the rate with which the active anethol molecules are formed. Both reactions are auto-accelerated during their initial stages,[24] and might, therefore, be considered as chain reactions. Furthermore, polymerizations, like auto-oxidations, are exothermic reactions and the heat of polymerization can be readily calculated, assuming the principle of additivity, from the heats of combustion of monomers and polymers. This has been done in Table V, using the only reliable existing data.[25]

TABLE V

COMPARISON OF HEATS OF COMBUSTION OF MONOMERS AND POLYMERS

Substances	Heats of combustion in kg.-cal.$_{15}$	Difference=heat of polymerization in kg.-cal.$_{15}$
Acrolein (3 moles)	1174.5	5.7
Metacrolein	1168.8	
Anthracene (2 moles)	3390.2	7.3
Dianthracene	3382.9	
n(Formaldehyde)	n(134.1)	n(12.0)
Paraformaldehyde	n(122.1)	
Acetaldehyde (3 moles)	839.1	26.3
Paracetaldehyde	812.8	
Cyanuramide (melamine)[26]	468.0	46.5
Cyanamide (3 moles)[26]	514.5	
Formaldehyde (3 moles)	402.3	73.8
a-Trioxymethylene	328.5	
Chlorocyanogen (3 moles)[26]	379.6	85.9
Cyanuric chloride[B]	293.7	
Acetylene (3 moles)	936.0	148.8
Benzene (g)	787.2	

These results seem to indicate that the total energy given off in auto-oxidations of the type here discussed should be attributed to both oxidation and polymerization reactions. It is quite probable, therefore, that a positive catalyst, such as benzoperacid, which is found to increase the oxygen absorption rate of anethol during the initial stages of the oxidation, will also be found to increase the polymerization rate. In any case,

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[24] For the rate of polymerization of styrene as determined by the rate of change of index of refraction with time, see Stobbe, Anlt., **409,** 8 (1915).

[25] "International Critical Tables," 1929, Vol. V, p. 163; Kharasch, ***Bureau** of **Standards Journal** of **Research, 2,*** 359 (1929).

[26] Lemoult, *Ann. chim. phys.,* [7] 16, 430 (1899).

a rapid polymerization during the initial stages of the oxidation of anethol will decrease its active concentration and cause the maximum oxygen absorption to occur long before an appreciable amount is actually oxidized. This will also account for the rapid falling off of the oxygen absorption rate in such reactions. It is quite possible, however, to find substances which will inhibit polymerization but allow the oxidation to proceed at a relatively high rate. This has been accomplished in the case of anthracene, anthraquinone and phenanthrenequinone. With hydroquinone and benzoquinone both oxidation and polymerization are considerably inhibited during the early stages of the reactions, but as soon as rapid oxidation sets in, polymerization also seems to proceed, since polymers have actually been isolated in these reactions.

Another conclusion which we are forced to draw from our experiments is that an inhibitor of auto-oxidation reactions does not necessarily have to be "a good reducing agent" or "an easily oxidizable" substance. It cannot be denied that both anthracene and phenanthrene are far better "reducing agents" or more "easily oxidized" than their respective quinones, yet their inhibitory effect on the oxidation of anethol is considerably lower than that produced by the quinones. Furthermore, anisaldehyde is an easily oxidized substance, yet its inhibitory effect is negligible.[27]

The author takes this opportunity to express his sincerest appreciation for the numerous suggestions and criticisms which he received from his closest associates and especially from Professor Lauder W. Jones of Princeton University, where the author carried out most of his preliminary experiments.

Summary

1. An improved method and apparatus have been described for the determination of oxygen absorption rates in auto-oxidation reactions, especially in oxidations in which gaseous products are being evolved.

2. The rates of oxygen absorption of iso-eugenol, iso-safrole, anethol + benzoperacid and anethol + various inhibitors have been measured at 110°.

3. It has been shown that the maximum oxygen absorption rate of anethol seems to be, within experimental error, equal to the sum of the maximum oxygen absorption rates of anisaldehyde and anethol + anthracene. Separation of the oxidation products showed that anthracene inhibits the oxidation of anisaldehyde selectively, while it is inducedly oxidized to anthraquinone.

4. The inhibitory constants of several inhibitors have been calculated, assuming a relationship connecting the maximum oxygen absorption rate, the time necessary for the rate to reach the maximum value and the concentration of the inhibitor used.

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[27] For further discussion of this point, see Milas, Ref. 7.

5. A tentative explanation has been given to account for the rapid falling off of the oxygen absorption rates long before an appreciable amount of the substance in question had undergone oxidation.

6. It has been pointed out that an inhibitor of the auto-oxidations studied in this investigation does not necessarily have to be a "good reducing" agent or an "easily oxidizable" substance. For example anthraquinone, which is not *oxidized during* the oxidation of anethol, is a far better inhibitor of this oxidation than anthracene, which is inducedly oxidized to anthraquinone.

CAMBRIDGE A, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 53]

THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. X. THE MEASUREMENT OF THE RELATIVE LABILITY OF BONDS BY MEANS OF RATES OF REACTIONS AND OF TEMPERATURES OF DECOMPOSITION. I. THE HYDROGEN–OXYGEN BOND IN CERTAIN ALCOHOLS

BY JAMES F. NORRIS AND RALPH C. YOUNG[1]

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Previous communications from this Laboratory have described the results of the study of the influence of structure on the lability of certain bondings between atoms in organic molecules. The method employed was to measure the relative rates at which the several members of a series of similar compounds reacted with a fixed reagent. The investigation in this way of a large number of alcohols gave definite results in regard to the influence of structure on the rates at which the hydrogen–oxygen linkage was broken, with the resulting replacement of hydrogen by the *p*-nitrobenzoyl radical.[2]

The results showed that the structure of the radical had a marked effect on the oxygen bond, RC—, in these compounds. It seemed desirable to study this bond by an entirely different method, to determine whether or not the effects shown were observable in transformations involving this bond that could be measured without the use of reaction velocities. A satisfactory method was found which involved the study of the action of heat on the triphenylmethyl ethers derived from a series of alcohols. Previous work[3] had shown that triphenylmethyl ethyl ether decomposes almost quantitatively, when heated, into triphenylmethane and acetaldehyde.

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[1] From the thesis of Ralph C. Young, presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1929.

[2] Norris and Ashdown, THIS JOURNAL, 47, 837 (1925); Norris and Cortese, *ibid.*, 49, 2640 (1927).

[3] Norris and Young, *ibid.*, 46, 2580 (1924).

$C_2H_5O—C(C_6H_5)_3 = CH_3CHO + (C_6H_5)_3CH$.—In this transformation the oxygen bond indicated was severed by heat. As the earlier work showed that this bond in the alcohols was greatly affected by changing the structure of the alkyl radical, it seemed probable that the members of a series of triphenylmethyl ethers would decompose at different temperatures when heated and that of two ethers the one containing the more stable oxygen linkage would break at the higher temperature.

The triphenylmethyl ethers derived from the alcohols were, accordingly, made and studied. It was found that in all cases the decomposition was definite. The ethers prepared from primary alcohols yielded aldehydes and those from secondary alcohols, ketones.

The temperature at which each ether started to decompose was measured with an accuracy of ±2°. The results are given in Table I, in which are also given the second-order velocity constants of the reactions between *p*-nitrobenzoyl chloride and the alcohols containing the radicals listed.

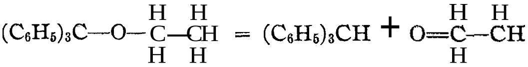
TABLE I

RESULTS OF EXPERIMENTS

Radical in ethers $(C_6H_5)_2C—OR$	Temp. (°C.) of decomposition	Velocity constant, p-$NO_2C_6H_5$-$COCl + H—OR =$ p-$NO_2C_6H_4$-$COOR + HCl$	Radical in ethers $(C_6H_5)_2C—OR$	Temp. (°C.) of decomposition	Velocity constant, p-$NO_2C_6H_5$-$COCl + H—OR =$ p-$NO_2C_6H_4$-$COOR + HCl$
Methyl	262	0.184	Iso-amyl	237	0.073
Ethyl	242	.085	*Sec.*-propyl	220	.010
n-Propyl	230	.066	*Sec.*-butyl	216	.0073
n-Butyl	239	.074	Benzyl	226	.017
Isobutyl	228	.031	β-Phenylethyl	236	.040

The results show that the two series of numbers follow in the same order, with but one exception. If we compare any two ethers, the one decomposing at the lower temperature is derived from the alcohol which reacts more slowly with the acyl chloride. This statement holds true in the case of 44 out of 45 of the possible comparison. The exception is in the case of the comparison of the β-phenylethyl and *n*-propyl radicals.

It is possible that in the decomposition of the ethers as indicated by the equation



$$(C_6H_5)_3C—O—\overset{H}{\underset{H}{C}}—\overset{H}{\underset{H}{C}}H = (C_6H_5)_3CH + O{=}\overset{H}{\underset{H}{C}}—\overset{H}{C}H$$

the lability of the carbon–hydrogen linkage shown is involved. The lability of the latter bond, necessarily, changes with the alteration of the structure of the alkyl radical, but it does not appear reasonable that the lability of this bond is the determining factor in the decomposition. It is a well-known fact that the carbon bond of the triphenylmethyl radical is very labile. Ethers which do not contain this radical undergo decomposition at relatively high temperatures. The most striking evidence, however, that the point of rupture of the molecule is at this bond is the fact that the temperatures at which decomposition takes place bear a definite relationship to the lability of the same oxygen linkage when measured by an independent method. When two series of data fall in the same or in the opposite order they must be related to the same cause.

It is a striking fact that the two sets of data change in the same direction with a change in the radical. This means that the oxygen linkage which reacts the more rapidly forms a compound which is more stable toward heat. Heat with a higher intensity factor (higher temperature) is required to break the bond. The results lead to the important conclusion, in the cases studied at least, that rates of reactions and temperatures of decomposition lead to the same conclusions in regard to the relative stability of the linkages between atoms.

The results indicated that the temperature at which a molecule begins to decompose when heated can be determined with a reasonable degree of definitiveness. As a result, work is now in progress in this Laboratory on the breaking of the C—H and C—C bonds by heat. Most work on the pyrolysis of organic compounds has been carried out at temperatures that produce the simultaneous splitting of several types of bonds, and, consequently, the results are not easily interpreted.

The fact that the triphenylmethyl alkyl ethers decomposed in such a simple way and at well-defined temperatures, and that in all probability the carbon–oxygen linkage was the one involved, offered an excellent opportunity of studying the effect of various types of substances on the temperature at which the bond breaks. In this way it was hoped to discover substances that possess the property of influencing the stability of this particular bond. The action of a number of elements and compounds is described later in this paper. It can be noted here that the temperature of decomposition of triphenylmethyl-ethyl ether was changed from 242 to 205° by ZnO, to 195° by $BaCl_2$, to 142° by $Al_2O_3 \cdot xH_2O$, to 132° by $KHSO_4$ and to room temperature by $AlCl_3$. The influence of the more active of these catalysts will be studied on other compounds containing the carbon–oxygen bond.

Work has been started on the determination of the temperatures at which esters derived from triphenylcarbinol decompose. In these compounds there are two types of C—O linkages: $(C_6H_5)_3C—O—COR$. It has been found that aluminum chloride breaks almost exclusively the oxygen bond to the triphenylmethyl radical, whereas anhydrous ferric chloride breaks largely the oxygen bond to the acyl radical. The results have led to a study of the selective action of catalysts on the more important bondings in organic compounds.

In the experimental part of this paper will be found an account of the investigation of the action of aluminum chloride on triphenylmethyl ethyl ether,

Experimental Part

Method of Obtaining Decomposition Temperatures of the Ethers.—A glass tube 1 cm. in diameter and 22 cm. long with side arm was connected with capillary tubing to a long horizontal capillary tube containing a column of mercury 1 cm. long. The tube together with a thermometer was supported in an oil-bath. A second oil-bath was also used and the whole was well protected from air drafts. As the temperature was raised the mercury was pushed along by the expanding air and its position was read off in millimeters from a scale at intervals of two degrees. By the plotting of

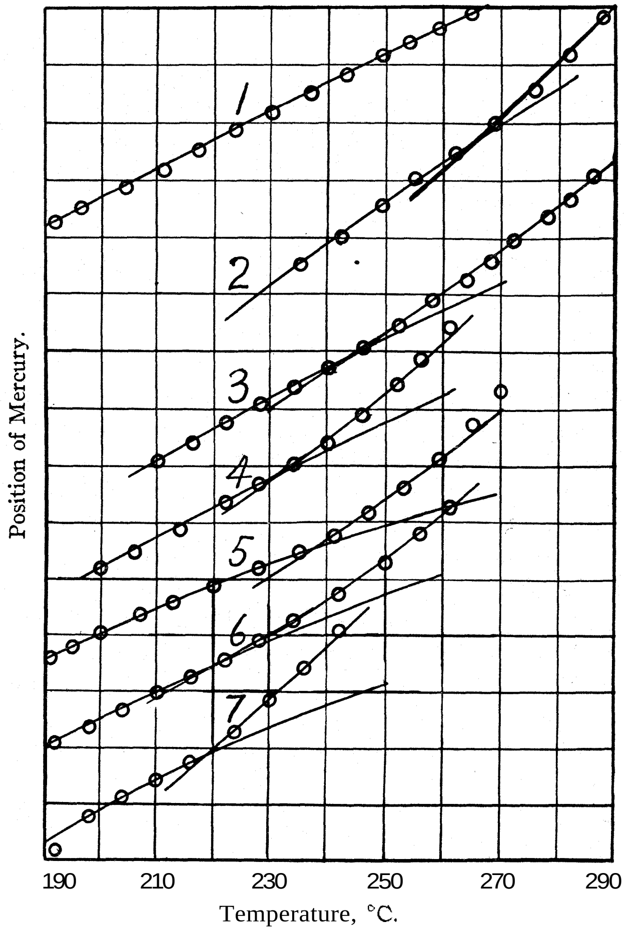


Fig. 1.—Position of mercury above an arbitrary zero for various values of the temperature. Each division = 2 cm. displacement. 1, Blank run; 2, triphenylmethyl methyl ether; 3, triphenylmethyl ethyl ether; 4, triphenylmethyl n-propyl ether; 5, triphenylmethyl n-butyl ether; 6, triphenylmethyl isopropyl ether; 7, triphenylmethyl *sec.*-butyl ether.

the positions of the mercury as ordinates against the temperatures as abscissas, a line connecting the points appeared as a smooth curve (Curve 1 in the chart). If, however, approximately 0.5 g. (0.0019 mole) of an ether were in the tube, when temperatures were reached at which decomposition occurred the gaseous product formed caused an increase in the rate at which the mercury moved, and the curves obtained had an inflection from which could be obtained the temperatures of decomposition. Since preliminary experiments showed that the ethers decomposed at about 200°, the heating was so regulated that 170° was reached in seventy-five minutes and from that temperature the rate was 1° per minute. About 60° below the temperature at which decomposition took place, the tube was closed by inserting a glass plug in a one-holed rubber stopper with which the tube was fitted. Readings were then taken. Approximate curves, plotted on a small scale, for six of the ethers are given in the accompanying chart. The decomposition temperatures given in Table II were obtained from large scale graphs and read to the nearest degree. Independent determinations are tabulated. Heating of the ethers in a silica tube seemed to cause no lowering of the decomposition temperature nor did a rate of heating one-half that given above.

TABLE II

RESULTS OF EXPERIMENTS

Radicals in ethers $(C_6H_5)_3C—O—R$	Decomposition temperature?, °C.			
Methyl	262	262	262	262
Ethyl	241	242	242	242
n-Propyl	230	230	230	
n-Butyl	238	239	240	
Isobutyl	227	228	227	
Iso-amyl	234	237	237	
Isopropyl	219	220	220	224
Sec.-butyl	216	216	214	
Renzyl	226	226		
β-Phenylethyl	236	237	236	***237***

Preparation of the Ethers.—The method of preparation of the ethers was similar to that of triphenylmethyl ethyl ether, in which case triphenylchloromethane was allowed to react with sodium ethylate in excess alcohol as the solvent.[3] After four hours of refluxing, the solvent was removed and the residue poured into water, taken up in ethyl ether and dried over calcium chloride. The method of purification of the crude product obtained from the ethyl ether solution will be given for the various ethers and also the results of the thermal decomposition (in Table III). Amounts recoverable from the mother liquors are not included in the yields given for the pure ethers. The results obtained in decomposing triphenylmethyl *n*-propyl ether are typical of the other ethers. From 20.9 g. of this ether there were obtained 2.5 cc. of a colorless liquid from 45 to 110°, 0.7 g. from 110 to 300" and 13 g. from 300 to 359°, the greater part of which distilled between 355 and 359°. The residue amounted to 2.5 g. The colorless liquid after fractionation gave a product boiling between 47 and 50°. By its boiling point, odor, test with fuchsine reagent and phenylhydrazone, it was identified as n-propionic aldehyde. The higher-boiling fractions which had solidified on cooling were crystallized from alcohol and triphenylmethane obtained in a yield of about 80%.

The Effect of Catalysts in Lowering the Decomposition Temperatures of Triphenylmethyl Ethyl Ether and Triphenylmethyl Methyl Ether.—Experiments were performed to find the lowest temperature to which it

TABLE III

ETHERS PREPARED, MELTING POINTS, BOILING POINTS AND ANALYTICAL DATA

	R in $ROC(C_6H_5)_3$	Crystallized from	Yield, %	°C.
1	CH_3-[4]	MeOH	55	M. p. 82.6–82.9
2	C_2H_5-[5]	Pet. ether and $(Et)_2O$	50	M. p. 81.2–81.8
3	$CH_3CH_2CH_2$-[6]	Pet. ether and *n*-PrOH	10	M. p. 50.5–52.5
4	$CH_3CH_2CH_2CH_2$-	(Fract. dist. in *vacuo*)	60	B. p. 212.8–213.0 (5 mm.)
5	$(CH_3)_2CH$-[7]	Pet. ether and $(Et)_2O$	50	M. p. 112.9–113.8
6	$CH_3CH_2CH(CH_3)$-	(Fract. extr. with pet. ether and fract. dist. in vacuo)	40	B. p. 196–198 (5 mm.)
7	$CH_3CH(CH_3)CH_2$-	Pet. ether and *iso*-BuOH	10	M. p. 51–53
8	$CH_3CH(CH_3)CH_2CH_2$-	(Fract. dist. in vacuo)	60	B. p. 205–205.5 (5 mm.)
9	$C_6H_5CH_2$-	Pet. ether and $(Et)_2O$	30	M. p. 103–104
10	$C_6H_5CH_2CH_2$-	Pet. ether and $(Et)_2O$	40	M. p. 87.1–87.8
11	$(p\text{-}CH_3C_6H_4)_3COC_2H_5$[8]	Ethyl ether	60	M. p. 111–112

No.	Carbon, % Calcd.	Carbon, % Found		Hydrogen, % Calcd.	Hydrogen, % Found		Prods. of thermal dec., triphenylmethane and
1	...	...	...	..	..	..	HCHO
2	...	...	...	..	..	..	CH_3CHO
3	87.41	87.27	87.17	7.28	7.27	7.14	CH_3CH_2CHO
4	87.34	87.37	87.07	7.59	7.58	7.56	$CH_3CH_2CH_2CHO$
5	87.41	87.31	87.49	7.28	7.51	7.44	CH_3COCH_3
6	87.34	87.73	87.70	7.59	7.88	7.39	$C_2H_5COCH_3$
7	87.34	87.39	87.38	7.59	7.76	7.75	$(CH_3)_2CHCHO$
8	87.27	87.08	87.12	7.87	7.93	7.88	$(CH_3)_2CHCH_2CHO$
9	89.14	88.93	88.98	6.28	6.39	6.49	C_6H_5CHO
10	89.01	88.91	88.87	6.59	6.83	6.84	$C_6H_5CH_2CHO$
11	...	...	...	..	..	..	CH_3CHO, $(p\text{-}CH_3C_6H_4)_3CH$[a]

[a] No triphenylmethane formed. On account of the lack of agreement in the literature as to the boiling and melting points of tritolylmethane, it was impossible to identify the white solid hydrocarbon (m. p. 62") as such.

was necessary to heat triphenylmethyl ethyl ether and triphenylmethyl methyl ether to obtain tests for aldehyde by means of fuchsine reagent and also by odor. One gram of the ether was heated in a tube supported in the vapors of a boiling liquid and *a* slow stream of carbon dioxide swept out any gaseous products of decomposition into a tube cooled in ice water to which could be added fuchsine solution at the end of one-half hour. It was customary also to have this tube connected with a second containing fuchsine solution through which the carbon dioxide was allowed to bubble. On account of the removal of the sulfur dioxide by the car-

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[4] Prepared by Friedel and Crafts, Ann. *chim. phys.*, [6] 1, 502 (1884).

[5] Norris and Young, Ref. 3.

[6] Prepared by Mamontow from *n*-propyl alcohol, triphenylchloromethane and sulfuric acid [J. Russ. *Phys.-Chem. Soc.*, 29, 233 (1887)].

[7] Prepared by Helferich, Speidel and Toeldte from isopropyl alcohol and triphenylchloromethane in pyridine [**Ber.**, **56B,** 766 (1923)].

[8] Prepared by Tousley and Gomberg, Am. *Chem.* J., **26,** 1518 (1904).

bon dioxide, a pink color would develop but the rate was slow unless aldehyde was present. It was found that if a test for aldehyde was obtained by the fuchsine the odor could also be detected, and the reverse was also true. Half-gram portions of several inorganic compounds were added to 1 g. of the ether in separate experiments to determine what effect they would have on the temperature necessary for the production of aldehyde and triphenylmethane as the latter compound was also identified. In tabular form are given the catalysts and the temperature required for the production of aldehyde.

Catalyst	Temp., °C.	Catalyst	Temp., °C.
For Triphenylmethyl Ethyl Ether		Na_2HPO_4	195
No catalyst	242	$Al_2O_3 \cdot xH_2O$ dried at red heat	183
Finely divided copper	215	$Al_2O_3 \cdot xH_2O$ dried at 180°	142
$Fe_2O_3 \cdot xH_2O$ dried at room temp.	205	$KHSO_4$	132
$Fe_2O_3 \cdot xH_2O$ dried at 170°	205	For Triphenylmethyl Methyl Ether	
$Fe_2O_3 \cdot xH_2O$ dried at red heat	205	No catalyst	267
ZnO	205	Finely divided copper	242
$Fe_2O_3 \cdot xH_2O \cdot ZnO$ dried at 170°	195	$Al_2O_3 \cdot xH_2O$	205
CuO	195	$Al_2O_3 \cdot xH_2O$	157
$BaCl_2$	195	$KHSO_4$	132

Action of Aluminum Chloride on Triphenyl Ethyl Ether.—Triphenylmethyl ethyl ether in carbon disulfide solution reacts with aluminum chloride free from hydrochloric acid to produce triphenylchloromethane and an aluminum chloro-ethylate.

$$2(C_6H_5)_3COC_2H_5 + 2AlCl_3 \longrightarrow (C_6H_5)_3CCl + (C_6H_5)_3CCl \cdot AlCl_3 + Al(OC_2H_5)_2Cl$$

To a solution of **28.8** g. (**0.1** mole) of triphenylmethyl ethyl ether in **75** cc. of carbon disulfide in an Erlenmeyer flask with drying tube was added **13.5** g. (**0.1** mole) of $AlCl_3$. Reaction began immediately, as evidenced by a slight warming and a darkening in the neighborhood of the aluminum chloride. After standing for twenty-four hours the carbon disulfide was decanted, filtered and evaporated; **15.6** g. of solid was obtained which was extracted with hot benzene. About **2** g. was insoluble in benzene. The soluble portion was found to be triphenylchloromethane. The residue in the reaction flask after decomposition with cracked ice yielded **11.6** g. of triphenylchloromethane.

It has been shown that $(C_6H_5)_3CCl \cdot AlCl_3$ reacts with ethers to give triphenylmethane.[3] If this molecular compound was formed as given in the equation, an additional amount of ether should give triphenylmethane; such proved to be true. An experiment similar to the one cited above was carried out, in which case, however, after the removal of the carbon disulfide by decantation, a second portion of the ether in carbon disulfide was added to the residue in the flask. After reaction there were obtained triphenylmethane and a tarry product. A third and fourth portion of the ether failed to undergo any change.

The material described as insoluble in benzene, which was obtained after the evaporation of the filtered carbon disulfide solution together with triphenylchloromethane, proved to be an almost white solid soluble in water. The aqueous solution gave positive tests for alcohol, chlorine and aluminum.

Anal. Calcd. for $Al(OC_2H_5)_2Cl$: Al, 17.75; Cl, 23.26. Found: Al, 17.40, 17.54; Cl, 23.65, 23.71.

Reaction of Ferric Chloride with Triphenylmethyl Ethyl Ether.—Ferric chloride brings about a decomposition of this ether different from that observed in the case of aluminum chloride. In the latter case the carbon-oxygen linkage to the triphenylmethyl radical is completely broken and triphenylchloromethane is formed. With ferric chloride about one-half of the product was triphenylcarbinol, in which this linkage remained intact.

Eleven and four-tenths grams (0.07 mole) of anhydrous ferric chloride and 20.2 g. (0.07 mole) of triphenylmethyl ethyl ether were allowed to react in 75 cc. of carbon disulfide. There was obtained 8 g. of material from the decanted carbon disulfide solution; this proved to be triphenylmethane and a tarry product. From the residue in the flask there was obtained 10 g. of triphenylcarbinol. When the reacting compounds were mixed in the proportion of 1 mole of ferric chloride to 3 moles of the ether, there was obtained besides triphenylmethane and triphenylcarbinol an amount of unchanged ether that indicated that the reaction took place between 1 mole of the ferric chloride and 1 mole of the ether.

Reaction of Aluminum Chloride and Ferric Chloride with Triphenylmethyl Acetate.—Fifteen and one-tenth grams (0.05 mole) of triphenylmethyl acetate was treated in carbon disulfide solution with 6.6 g. (0.05 mole) of aluminum chloride in the same manner as in the case of triphenylmethyl ethyl ether. Nine grams of solid was obtained from the carbon disulfide solution, which on crystallization from petroleum ether yielded triphenylchloromethane. The residue in the reaction flask was decomposed with ice and an additional four grams of triphenylchloromethane was collected. An experiment was carried out similarly in which ferric chloride was used instead of aluminum chloride. Triphenylcarbinol was the product of the reaction.

Summary

1. The products of the pyrolysis of ethers of the type $(C_6H_5)_3C-OR$ were shown to be triphenylmethane and either an aldehyde or ketone, formed as the result of the loss of hydrogen by the OR group. The temperatures at which decomposition occurs were found to vary with the structure of the alkyl radical. Change in this radical resulted in an alteration of the lability of the bond between oxygen and the triphenylmethyl group. If the ethers are arranged according to decreasing stability toward heat, the alkyl radicals fall in the order methyl, ethyl, n-butyl, isoamyl, β-phenylethyl, n-propyl, isobutyl, benzyl, isopropyl, *sec.*-butyl. This order, with one exception, is the same as that obtained as the result of the study of the lability of the oxygen bond in alcohols (H–OR) as measured by the velocity of the reactions between the latter and p-nitrobenzoyl chloride. The two independent methods based on different types of reactions lead to the same conclusion as to the effect of radicals on the lability of bonds.

2. The temperatures required to cause the decomposition of the ethers were found to be markedly affected by catalytic agents. The selective

action of catalyst in breaking a particular bond was shown by the action of aluminum chloride and ferric chloride on triphenylmethyl acetate: the former produced triphenylchloromethane and the latter triphenylcarbinol.

3. Aluminum chloride reacts with triphenylmethyl ethyl ether in the cold, the products being $(C_6H_5)_3CCl$ and $Al(OC_2H_5)_2Cl$.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

SOME HIGHLY PHEMYLATED ALIPHATIC NITRO COMPOUNDS

BY E. P. KOHLER AND J. F. STONE, JR.

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Although aliphatic nitro compounds have been the subject of many excellent investigations they still present a number of problems of theoretical interest. Little is known about the factors that influence the stability of the *aci* forms and the manner in which these pass into true nitro compounds, the extent to which the nitro and iso-nitro groups are modified by conjugation with ethylenic linkages, the intimate structure of nitro and iso-nitro groups. Since the life of the *aci* forms of simple nitro compounds is short, we have studied a number of phenylated derivatives in the expectation that the saturated representatives would be more tractable than the simpler compounds which have been studied heretofore, and that a comparison between the unsaturated members and the correspondingly phenylated carbonyl compounds would be instructive.

Our starting materials were nitro styrene and nitro stilbene. Owing to the ease with which it polymerizes, the former proved comparatively useless for our purpose, but the latter enabled us to prepare and study still more highly phenylated saturated and unsaturated nitro compounds. It reacts with phenyl magnesium bromide as readily as does the corresponding unsaturated ketone—benzaldesoxybenzoin—and like the unsaturated ketone it forms, apparently exclusively, a 1,4-addition product

$$\underset{\text{I}}{C_6H_5CH{=}C(C_6H_5)NO_2} \longrightarrow \underset{\text{II}}{(C_6H_5)_2CHC(C_6H_5){=}N(OMgBr)O} \longrightarrow \underset{\text{III}}{(C_6H_5)_2CHC(C_6H_5){=}N(OH)O}$$

From the product of the Grignard reaction it is easy to secure the corresponding *aci* nitro compound. In its chemical reactions this iso-nitro compound closely resembles its simpler analogs; it forms sodium, copper and silver salts; it gives the characteristic color reactions with ferric chloride and phenyl diazonium chloride; and it reacts with bromine in the usual manner. But this iso-nitro compound differs much from its simpler analogs both in the degree and in the quality of its instability. It can be isolated without too much difficulty in the form of a crystalline solid, which, when perfectly pure, may undergo relatively little change for several weeks. Its persistence varies greatly with its purity, hence it deteriorates more rapidly in a closed vessel than in the open or in a vacuum, more rapidly also in solution than by itself. In the end all specimens degenerate into red oils.

While this iso-nitro compound, like all others, is unstable, it exhibits little if any tendency to undergo spontaneous rearrangement into a true nitro compound. The oily degradation products, whether formed from the solid or in solution, contain barely a trace of the isomer. They are composed largely of triphenyl ethylene, triphenyl ethanone and triphenylethanone oxime, but contain a number of other substances—products which are due to intramolecular oxidation and reduction, and to hydrolysis.

$$\underset{\text{IV}}{(C_6H_5)_2C{=}CHC_6H_5} \longleftarrow (C_6H_5)_2CHC(C_6H_5){=}N(OH)O \longrightarrow$$

$$\underset{\text{V}}{(C_6H_5)_2CHC({=}NOH)C_6H_5} \longrightarrow \underset{\text{VI}}{(C_6H_5)_2CHCOC_6H_5}$$

Another peculiarity of the nitro compound that seems at first surprising, is that its isomerization to the true nitro compounds is not promoted by acids; weak acids and very small concentrations of strong acids appear to retard deterioration and strong acids promote hydrolysis to triphenyl ethanone. In order to bring about isomerization it is necessary to employ bases. Strong bases like sodium hydroxide form salts that are sparingly soluble and apparently perfectly stable in strongly alkaline solutions. But when a dilute aqueous solution of such a salt is kept, it gradually becomes cloudy and more alkaline, and in time it deposits an equivalent quantity of the true nitro compound. The process is accelerated by boiling and it takes place rapidly when an organic base is added to a methyl alcoholic solution of the *aci* nitro compound.

The α-bromo substitution product of the true nitro compound is readily obtained by the action of bromine on the *aci* form, its sodium salt, or the magnesium halide derivative that is formed in the Grignard reaction. It is also easy to eliminate hydrogen bromide from it, and thus obtain a phenylated nitro stilbene—triphenyl nitro ethylene

$$(C_6H_5)_2CHC(C_6H_5){=}N(OH)O \longrightarrow \underset{\text{VII}}{(C_6H_5)_2CHCBr(C_6H_5)NO_2} \longrightarrow$$

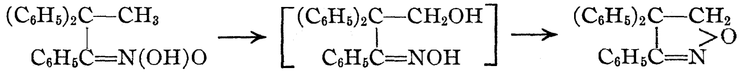
$$\underset{\text{VIII}}{(C_6H_5)_2C{=}C(C_6H_5)NO_2}$$

We tried in vain to introduce a fourth phenyl group into triphenyl nitro ethylene, but had no difficulty in introducing methyl, ethyl and benzyl groups. In contrast with the corresponding unsaturated ketone, $(C_6H_5)_2C{=}C(C_6H_5)COC_6H_5$, the unsaturated nitro compound combines readily with aliphatic magnesium compounds, and despite the accumulation of phenyl groups about the conjugated system the reaction consists, apparently exclusively, of 1,4-addition. After acidification the product is in each case an iso-nitro compound

$(C_6H_5)_2C(CH_3)C(C_6H_5){=}N(OH)O$ IX $\qquad$ $(C_6H_5)_2C(C_2H_5)C(C_6H_5){=}N(OH)O$ X

$(C_6H_5)_2C(CH_2C_6H_5)C(C_6H_5){=}N(OH)O$ XI

These new aci nitro compounds, the most highly branched aliphatic nitro compounds that are known, behave in the main like *aci*-triphenyl nitro ethane. They give nearly all the characteristic reactions of the simplest *aci* nitro compounds but they do not react normally with bromine and for some unknown reason it was also impossible to make well-defined bromine compounds by the action of bromine on their metallic derivatives. Like all other *aci* nitro compounds they rapidly deteriorate both by themselves and in the presence of acid, but under these conditions they neither undergo rearrangement to true nitro compounds like the simple nitro paraffins, nor hydrolysis to the corresponding ketone like aci-triphenyl nitro ethane. The readjustment is involved, and it leads to more than one substance, but the principal product is a cyclic compound that is doubtless due to internal oxidation and reduction. Thus when hydrochloric acid is added to a methyl alcoholic solution of aci-triphenyl nitro propane, 70% of the product is triphenyl isoxazoline



$$\begin{matrix}(C_6H_5)_2C-CH_3\\ |\\ C_6H_5C{=}N(OH)O\end{matrix} \longrightarrow \left[\begin{matrix}(C_6H_5)_2C-CH_2OH\\ |\\ C_6H_5C{=}NOH\end{matrix}\right] \longrightarrow \begin{matrix}(C_6H_5)_2C-CH_2\\ |\qquad >O\\ C_6H_5C{=}N\end{matrix}$$

XII

All the true nitro compounds that we have studied are perfectly stable both in solid form and in solution. A solution of tetraphenyl nitro propane in pure dry ether has not undergone any change in the three years during which it has been kept under observation. Since, in ethereal solution, the iso-nitro compound completely disappears in a few weeks, it seems reasonable to conclude that this solution contains no *aci* form whatsoever and that the true nitro compounds do not spontaneously undergo rearrangement.

From a study of these substances we have, therefore, reached the conclusion that the scheme

$$(R)_2\,CHNO_2 \rightleftharpoons (R)_2\,C{=}N(OH)O$$

does not represent reality. No quantitative results are available but, since the *iso* form is an acid, our qualitative results appear to be in complete accord with Lowry's mechanism for such rearrangements.

Experimental Part

I. Experiments with Nitro Stilbene

Nitro stilbene reacts readily both with methylmagnesium iodide and with phenyl magnesium bromide. Since the reaction with methyl magnesium iodide gave no well-defined product it will not be described. In the case of phenyl magnesium bromide at least 90% of the reaction consists in 1,4-addition to the conjugated system C=C—N=O. This follows not only from the fact that the resulting magnesium derivative is a salt of an acid which gives all the characteristic reactions of iso-nitro compounds, but also from a series of transformations which show that the phenyl group goes into the β-position.

$$\underset{\text{II}}{(C_6H_5)_2CHC(C_6H_5){=}NO(OMgBr)} \longrightarrow (C_6H_5)_2CHC(C_6H_5)BrNO_2 \longrightarrow$$

$$(C_6H_5)_2C{=}C(C_6H_5)NO_2 \longrightarrow (C_6H_5)_2CO$$

While it is possible to isolate pure iso-nitro compound by manipulating the reaction mixture which contains the magnesium derivative II in the usual manner, it is much better to secure it by way of the sodium salt. The procedure finally adopted was as follows.

A solution obtained by dissolving 12 g. of magnesium in 80 g. of bromobenzene and 500 cc. of ether was cooled in ice water. To this solution was added, gradually, with constant cooling and stirring, 60 g. of finely ground nitro stilbene. The resulting clear liquid was boiled for fifteen minutes, then cooled again and diluted with an equal volume of chilled low-boiling petroleum ether. The unused Grignard reagent, diphenyl, and other impurities remained in solution, while fairly pure magnesium derivative was precipitated as a pale yellow paste which generally solidified. After decanting the ether–petroleum ether layer and replacing it with 100 cc. of alcohol-free ether, the magnesium derivative was decomposed with iced acid and the ethereal layer separated and washed in the usual manner. When this ether solution was shaken with 10% aqueous sodium hydroxide it yielded an almost perfectly pure, colorless, crystalline sodium salt of the iso-nitro compound.

For the purpose of isolating the iso-nitro compound itself, the ethereal layer was decanted and replaced with fresh alcohol-free ether, the mixture cooled in a freezing mixture and gradually acidified with excess of iced hydrochloric acid. The resulting ethereal solution when dried for a few minutes with calcium chloride and then concentrated under diminished pressure deposited pure iso-nitro compound. The yield was 90%.

Anal. Calcd. for $C_{20}H_{17}O_2N$: C, 79.2; H, 5.6. Found: C, 79.1; H, 5.4.

Aci-triphenyl-nitro-ethane (III) crystallizes in colorless prisms and melts, with decomposition, at about 91°. It is readily soluble in all common organic solvents except petroleum ether. When it is prepared from the sodium salt as described and kept in an open vessel it may remain solid for as long as several weeks, but when it is made directly from the magnesium derivative it generally turns to a red oil within twenty-four hours. The change is promoted by organic solvents and other impurities. When the pure solid is suspended in dilute hydrochloric acid it disintegrates more slowly than when it is kept by itself. Solutions of the iso-nitro compound in organic solvents generally become distinctly colored in twenty-four hours, and after a week they fail to give the delicate color reaction with ferric chloride.

The Sodium Salt, $(C_6H_5)_2CHC(C_6H_5){=}NO{-}ONa$.—The *aci* form of triphenyl nitro ethane is readily soluble in sodium carbonate as well as sodium hydroxide, forming a sodium salt that precipitates at once from the hydroxide and more slowly from the carbonate. It is soluble in alcohols and in acetone but is best purified by recrystallization from water, in which it is only moderately soluble at low temperatures.

Anal. Calcd. for $C_{20}H_{16}O_2NNa$: Na, 7.1. Found: Na, 7.4, 7.0.

The sodium salt crystallizes in downy needles, melts at 100–103°, and is not altered by heating to 120°. As it is stable it constitutes a convenient means of stocking the *aci* nitro compound.

Other Salts.—When a drop of ferric chloride solution is added to an ethereal solution of the *aci* nitro compound, it immediately produces a red color which is destroyed by addition of hydrochloric acid and regenerated when the acid is partially neutralized by bases. This reaction which is characteristic of iso-nitro compounds supplies a delicate method for observing the disappearance of the *aci* form in solution.

The *aci* nitro compound also readily forms a copper salt, which is obtained as a colorless crystalline precipitate when an ethereal solution is shaken with copper acetate and when an ethereal solution of the *aci* compound is added to methyl magnesium iodide it liberates methane and precipitates colorless magnesium halide similar to that obtained in the Grignard reaction.

Attempts to **Alkylate.**—A suspension of the sodium salt in anhydrous ether was boiled for eight hours with excess of methyl iodide, then filtered. The filtrate on concentration deposited a crystalline solid which after recrystallization from methyl alcohol melted at **173°**.

Anal. Calcd. for $C_{20}H_{17}ON$: C, **83.6;** H, 5.9. Found: C, **83.0;** H, 5.7.

The composition and melting point indicated triphenyl ethanone oxime (V) and the identification was completed by comparison with a specimen made from the ketone. A repetition of the experiment, using methyl alcohol as solvent, likewise gave mainly oxime but along with it a small quantity of the true nitro compound due to rearrangement in the slightly basic medium. Instead of being alkylated, therefore, the sodium salt was merely reduced to the corresponding oxime.

Oxidation and Reduction.—A freshly prepared solution of the iso-nitro compound in ethyl bromide is not attacked by ozone and an aqueous solution of the sodium salt is not oxidized by a **10%** solution of sodium peroxide. Aqueous solutions of the sodium salt reduced permanganate but gave only oily products. Solutions of the iso-nitro compounds in moist ether were readily reduced by aluminum amalgam and gave triphenyl ethanone oxime as the primary product but the process was either accompanied or followed by condensation reactions which gave intractable substances.

Hydrolysis.—Cold concd. hydrochloric acid was added slowly and with constant cooling to a freshly made ethereal solution of 2 g. of the iso-nitro compound until there were two distinct layers. The mixture was shaken for ten minutes, and then cautiously diluted. The ethereal layer on evaporation left **1.75** g. of practically pure triphenyl ethanone, which was identified by comparison with a sample on hand. The same process occurred when a methyl alcoholic solution of the sodium salt was acidified with excess of concentrated hydrochloric acid and kept at 50° for several hours, but the product was less pure and the yield smaller. Since no true nitro compound could be detected in either case it is evident that mineral acids readily hydrolyze but do not promote the rearrangement of the iso form.

Rearrangement to the **True** Nitro Compound.—A solution of 5 g. of the pure sodium compound in one liter of water was boiled for an hour, during which a solid separated in pale yellow crystals. The suspension was filtered and the feebly alkaline filtrate tested for unchanged *aci* nitro compound by acidification, extraction with ether and addition of ferric chloride to the ethereal extract. The *aci* nitro compound had disappeared completely.

The solid was washed with water and recrystallized from methyl alcohol. It separated in rectangular elongated prisms which were faintly yellow in color and melted at 130°. The yield was 90%.

Anal. Calcd. for $C_{20}H_{17}O_2N$: C, **79.2;** H, 5.6. Found: C, **79.2**; **H,** 5.6.

α,β,β-Triphenyl nitro ethane is readily soluble in acetone, in alcohol and in ether, very slightly soluble in petroleum ether, and insoluble in water. It separates from petroleum ether in colorless prisms but it is most conveniently recrystallized **from** methyl alcohol. Its ethereal solution does not develop any color when treated with ferric chloride, and it neither dissolves in dilute sodium hydroxide nor is extracted from ethereal solution by concd. alkalies.

Change from Nitro to Iso-nitro Compound.—While the nitro compound is not extracted from its ethereal solution by aqueous sodium hydroxide, it is rapidly removed by methyl alcoholic sodium methylate. Thus after an ether–petroleum ether solution containing **2** g. of the substance had been shaken for five minutes with **10** cc. of a concentrated solution of sodium methylate, it was found to be entirely free from nitro compound. By allowing the pale yellow alcoholate solution to evaporate and treating the residue with ice water, it was easy to isolate a sodium salt that on acidification gave the *aci* nitro compound in a yield of about 90%.

α,β,β-Triphenyl-α-bromo-nitro Ethane (VII).—Triphenyl nitro ethane does not react with bromine but its α-bromo derivative is readily made from the *aci* form or its sodium salt. It is most economical, however, to prepare the bromo compound by adding bromine to the ethereal solution that is obtained when nitro stilbene is added to phenyl magnesium bromide. Thus, in a typical case, the solution obtained by adding **60** g. of nitro stilbene to the requisite amount of phenyl magnesium bromide was boiled for fifteen minutes, then cooled in a freezing mixture and treated with **82** g. of dry bromine. The bromine was added drop by drop while the solution was stirred vigorously. It first produced a greenish-brown paste which was gradually converted into a fine crystalline solid as the reaction neared completion. After all the bromine had been added, the stirring was continued for another half hour, during which the temperature was allowed to rise. The solid was collected on a suction filter, washed with ether and recrystallized from acetone; yield, 95%.

Anal. Calcd. for $C_{20}H_{16}O_2NBr$: C, 62.8; H, **4.2.** Found: C, **62.7;** H, 4.6.

The bromo compound is very sparingly soluble in all common organic solvents except hot acetone. It crystallizes in small colorless prisms and melts with decomposition at 185°. It readily reacts with ethyl magnesium bromide and forms the magnesium bromide salt of *aci* triphenyl nitro ethane—an interesting transformation. When it is heated above the melting point it loses nitrous acid and passes into bromo triphenyl ethylene, but when it is digested with alcoholates it loses hydrogen bromide and forms the corresponding unsaturated nitro compound—triphenyl nitro ethylene.

II. Experiments with Triphenyl Nitro Ethylene

Preparation.—A suspension of **75** g. of the bromo compound described in the preceding paragraph in a solution obtained by dissolving **25 g.** of sodium in **500** cc. of methyl alcohol was boiled for an hour, during which the colorless compound was replaced by a granular yellow precipitate. The solid was washed with water, methyl alcohol and ether, and then recrystallized from acetone; yield, **56** g.

Anal. Calcd. for $C_{20}H_{15}O_2N$: C, **79.7;** H, **5.0.** Found: C, **79.8;** H, **5.2.**

The nitro compound crystallizes in yellow prisms which melt at 170° and decompose a few degrees above the melting point. It is very sparingly soluble in alcohol and ether, moderately soluble in acetone.

Oxidation and Reduction.—In order to verify the structure, the nitro compound was both oxidized and reduced. It was readily oxidized both by chromic acid in glacial acetic acid and by ozone in chloroform. In each case the principal product was benzophenone. For the purpose of reduction **6** g. of zinc dust was gradually added to a boiling solution of **5** g. of the substance in **50** cc. of glacial acetic acid and **15** cc. of water. When all the color had disappeared the solution was poured into water. It precipitated a colorless nitrogen-free solid that after recrystallization melted at 136° and formed an oxime melting at 172°. The physical properties of the substance agree with those of triphenyl ethanone, but the melting point of the oxime is 10° below that given for the oxime of this ketone.[1] The oxime was, therefore, analyzed and, finally, to remove all doubt, triphenyl ethanone was prepared in a different manner and turned into oxime as directed by Kohler. The oxime thus obtained likewise melted at 172°, and a mixed melting point of the two preparations proved their identity. Zinc and acetic acid, therefore, reduce the unsaturated to the saturated nitro compound, which is then hydrolyzed to the corresponding ketone

$$(C_6H_5)_2C{=}C(C_6H_5)NO_2 \longrightarrow (C_6H_5)_2CHC(C_6H_5){=}NO{-}OH \longrightarrow (C_6H_5)_2CHCOC_6H_5$$

Reaction with Grignard Reagent.—At the temperature of ice water the finely ground nitro compound readily reacts with alkyl magnesium halides without evolution of gas; the solutions remain colorless but deposit a colorless crystalline derivative, the reaction is confined to the conjugated system, and the yield is in excess of 90%; but if the temperature is allowed to rise, the nitro group also becomes involved, gas is given off, the solution becomes yellow, and the yield falls off. The solution also slowly turns yellow when it is allowed to stand overlong at low temperatures but this appears to be due to a slow decomposition of the iso-nitro compounds and has only a slight effect on the yields. A typical procedure is illustrated by the following experiment with methyl magnesium iodide.

Ten grams of the finely ground nitro compound was slowly stirred into an ice cold solution prepared from **3.2** g. of magnesium, 18 g. of methyl iodide and 150 cc. of ether. As soon as the mixture had become colorless it was decanted into iced hydrochloric acid. The ethereal layer, when shaken vigorously, began to deposit the iso-nitro compound as a pale pink crystalline solid. The deposition was rapidly made as complete as possible, by addition of cold petroleum ether. The solid was collected on a filter and the ether–petroleum ether extracted with 10% aqueous sodium hydroxide. The solid was washed with water and ether and recrystallized from ether–petroleum ether; yield, 8 g. The combined sodium hydroxide extracts, treated in the usual manner, gave nearly 1 g. more of less pure compound.

The properties of the products obtained with the three magnesium compounds are summarized in the following table.

		Composition, %			M. p., °C.	Yield,
Reagent	**Formula**	**C**	**H**	**N**	**(dec.)**	**%**
CH_3MgI	$(C_6H_5)_2C(CH_3)C(C_6H_5)N(OH)O$	79.3	6.2	4.6	120	88
	$(C_6H_5)_2C(CH_3)CH(C_6H_5)NO_2$	79.0	5.8		136	95
C_2H_5MgI	$(C_6H_5)_2C(C_2H_5)C(C_6H_5)N(OH)O$	79.0	6.1		120	85
	$(C_6H_5)_2C(C_2H_5)CH(C_6H_5)NO_2$	79.5	6.3		138	95
$C_6H_5CH_2MgI$	$(C_6H_5)_2C(CH_2C_6H_5)C(C_6H_5)N(OH)O$	82.0	6.2		140	85
	$(C_6H_5)_2C(CH_2C_6H_5)CH(C_6H_5)NO_2$	82.1	6.0		136	95

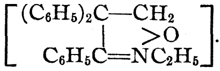
The stability relationships of these iso-nitro compounds are practically the same as those of nci-triphenyl nitro propane, as is also their behavior toward acids and bases, oxidizing, reducing and alkylating agents; only their behavior toward hydrolytic agents is different.

[1] Kohler, *Am. Chem. J.*, ***36,*** 193 (1906).

Action of Methyl Alcoholic Hydrochloric Acid, **3,4,4-Triphenyl** Isoxazoline, **XII.**—A solution of 3 g. of the sodium salt in methyl alcohol was slowly added to a mixture of 150 cc. of absolute methyl alcohol and 120 cc. of concentrated hydrochloric acid which was stirred mechanically and kept at 50° for three hours. The light red reaction mixture was diluted with water and allowed to stand overnight. Since it yielded no solid product, it was extracted with ether. The ethereal solution was washed with sodium carbonate and water, dried with calcium chloride and concentrated. It deposited colorless needles which after one recrystallization from ether melted at 142°.

Anal. Calcd. for $C_{21}H_{17}ON$: mol. wt., 299; C, 84.2; H, 5.7. Found: mol. wt., 301; C, 83.9; H, 5.8.

The substance is remarkably stable and unreactive. It does not react with permanganate and it is not attacked by ozone. It was recovered after it had been boiled with sodium methylate and also after it had been dissolved in cold concentrated sulfuric acid or heated for fifteen minutes with 80% sulfuric acid on a steam-bath.

Ethylation of the Isoxazoline, 

$$\left[\begin{array}{l}(C_6H_5)_2C—CH_2 \\ \qquad\quad | \qquad >O \\ \quad C_6H_5C{=}NC_2H_5\end{array}\right].FeCl_4$$

—A solution of 0.5 g. of the isoxazoline in **3** g. of diethyl sulfate was heated for three hours at 120°, then diluted with hydrochloric acid and boiled for a few minutes to decompose the excess of sulfate. The clear solution was extracted with ether, then treated with 1 cc. of concd. ferric chloride. This precipitated an oil which soon solidified. The yellow solid was recrystallized from ethyl bromide and ether. The yield of pure product was 0.52 g.

Anal. Calcd. for $C_{23}H_{22}ON{\cdot}FeCl_4$: C, 52.5; H, 4.2. Found: C, 53.0; H, 4.2.

The substance is sparingly soluble in ether, readily soluble in ethyl bromide. It crystallizes from a mixture of these solvents in needles, and melts at 110–111°. Alkalies convert it into an ether-soluble pseudo base from which it is regenerated by hydrochloric acid and ferric chloride.

Summary

1. This paper contains directions for preparing pure highly phenylated aliphatic nitro and iso-nitro compounds.
2. It shows that neither form spontaneously passes into the other, that solutions do not contain an equilibrium mixture of the two forms, and that acids do not promote the rearrangement of the *iso* to the normal form.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

CONDENSATION REACTIONS OF CYCLIC KETONES. II. THE FORMATION OF QUINOLINE DERIVATIVES FROM CERTAIN INDIGOIDS

BY ARTHUR J. HILL, ALFRED S. SCHULTZ AND HARRY G. LINDWALL

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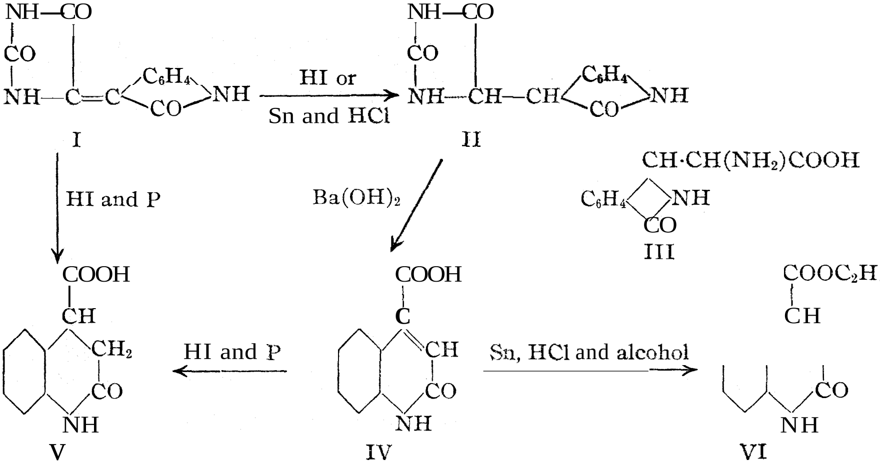
It has been shown by one of us[1] that hydantoin will condense with isatin, giving hydantoin-($\Delta^{5,3'}$)-oxindole, I. Hydrolysis of the reduction product, II, of this compound, should theoretically give oxindole-amino-acetic acid, III, and thus afford a new and convenient method for the synthesis of oxindole acids. This possibility was suggested in the previous paper[1] of this series.

However, we have now found that the hydrolytic reaction proceeds in abnormal fashion, and that the end-product is a quinoline derivative, the nature of which depends upon the type of hydrolytic agent used.[2]

Hydantoin-($\Delta^{5,3'}$)-oxindole reduces smoothly to hydantoin-5,3'-oxindole, II, by the action of tin and hydrochloric acid, or hydriodic acid in acetic acid medium. When the reduced indigoid, II, is hydrolyzed with barium hydroxide, the usual cleavage of the hydantoin ring takes place, but this is followed by profound decomposition, involving opening of the oxindole ring, deaminization and final closure to 2-quinolone-4-carboxylic acid, IV. This substance can be reduced to the saturated acid, V, by hydriodic acid and phosphorus, or by tin and an alcohol solution of hydrogen chloride, the ethyl ester, VI, of the reduced acid being produced by these latter reagents.



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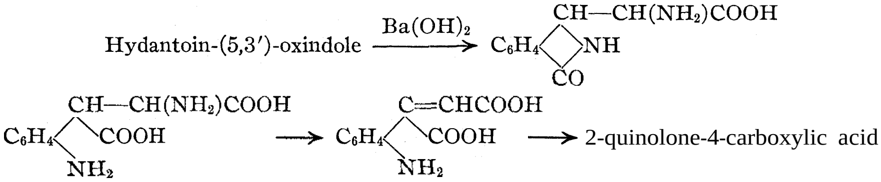
[1] Hill and Henze, THIS JOURNAL, 46, 2806 (1924).

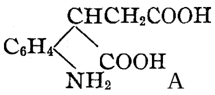
[2] Preliminary paper presented by Hill and Lindwall at the Philadelphia meeting of the American Chemical Society, September, 1926.

Indeed, hydantoin-(A$^{b,3'}$)-oxindole itself can be directly transformed into the saturated acid, V, 2-keto-1,2,3,4-tetrahydroquinoline-4-carboxylic acid, by treatment with hydriodic acid and red phosphorus.

The mechanism of the formation of 2-quinolone-4-carboxylic acid from hydantoin-(5,3′)-oxindole would appear to be as follows

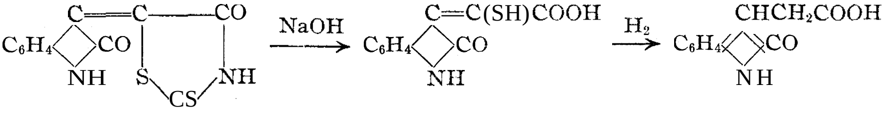


In the last step ring closure may theoretically take place to give either an indolinone or a quinoline ring depending on the carboxyl group which functions in the change. However, conditions favor the formation of the six-membered ring. A somewhat similar interpretation may be given to the reaction with hydriodic acid and red phosphorus. It would differ chiefly in having an additional step representing the formation of the saturated acid (A), which would be derived either from the corresponding unsaturated acid or from the amino acid. It will be observed that oxindole-acetic acid would have been formed had the closure involved the carboxyl group derived from the original isatin carbonyl group, or had the oxindole ring remained unbroken during the reaction. That the five-membered ring does not form will be demonstrated by a number of considerations.



A

Coincident with our discovery of these interesting reactions of hydantoin-(Δ$^{5,3'}$)-oxindole, Granacher[3] published an account of a procedure for making so-called oxindole-acetic acid, the starting material being β-rhodanal-oxindole, VII. His method is outlined as



VII Oxindole-acetic acid

The properties of our reduced acid, V (later shown to be a quinoline derivative), and also its derivatives, were identical with those of Granacher's oxindole-acetic acid and its derivatives. These facts were presented by two of us,[4] but with reservations regarding the correctness of the structural interpretations, having in mind the possibility of the cleavage of the oxindole ring during these reactions.

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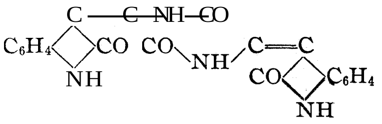
[3] Granacher and Mahal, *Helv. Chim. Acta*, 6, 467 (1923).

[4] Hill and Schultz, Washington Meeting of the American Chemical Society, April, 1924.

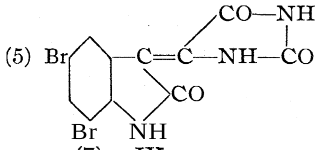
Accordingly we synthesized 2-quinolone-4-carboxylic acid by two well-known methods, first, by treating acetyl-isatin with sodium hydroxide[5] and, second, by condensing isatin with malonic acid.[6] The substance resulting from either of these two procedures was identical with our unreduced acid, IV, and the reduced acid derived from any one of the three sources was identical with Granacher's so-called oxindole-acetic acid. The end-product of our synthesis and also that of Granacher's is, therefore, 2-keto-1,2,3,4-tetrahydroquinoline-4-carboxylic acid, V. The correctness of our conclusions is further substantiated by Aeschlimann's[7] recent work, which also deals with the structure of 2-quinolone-4-carboxylic acid, and with Granacher's "oxindole-acetic acid."

The application of diketopiperazine to the preparation of 2-keto-tetrahydroquinoline-4-carboxylic acid was productive of results wholly similar to those obtained with hydantoin. The condensation of diketopiperazine with two molecules of isatin was readily accomplished in sodium acetate–acetic acid–acetic anhydride medium, the end-product, VIII, being acetylated by reason of the necessity of using a large excess of acetic anhydride in order to effect condensation.

On simultaneous reduction and hydrolysis of this compound with hydriodic acid and phosphorus, 2-keto-tetrahydroquinoline-4-carboxylic acid was formed.



VIII



IX

The writers have been successful in condensing 5-bromo- and 5,7-dibromo-isatin with both hydantoin and diketopiperazine. Owing to the fact that these highly colored indigoids are extremely insoluble, the study of their reduction and subsequent hydrolysis has been rendered difficult. However, it is significant that hydantoin-($\Delta^{5,3'}$)-5',7'-dibromoxindole, IX, is converted into 2-keto-tetrahydroquinoline-4-carboxylic acid by heating with phosphorus and hydriodic acid.

Experimental Part

Hydantoin-5,s'-oxindole (II) by the Reduction of Hydantoin-($\Delta^{5,3'}$)-oxindole

A. Reduction with Tin and Hydrochloric Acid.—Ten grams of hydantoin-($\Delta^{5,3'}$)-oxindole was suspended in 200 cc. of ethyl alcohol and after the addition of 13 *g.* of tin, hydrogen chloride was passed into the hot solution until the metal had dissolved. The indigoid was completely reduced after a second treatment with 13 g. of tin, followed by

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[5] Camps, *Arch. Pharm.*, 237,687 (1899).

[6] Borsche and Jacobs, *Ber.*, 47, 354 (1914).

[7] Aeschlimann, *J. Chem. Soc.*, 128,2902 (1926).

saturation of the solution with hydrogen chloride. The excess alcohol and acid was removed by distillation under diminished pressure and hydrochloric acid (10%) was added to the residual material. Acid was used in preference to water in order to prevent precipitation of basic tin compounds. Hydantoin-(5,3′)-oxindole separated from this solution upon standing. It was filtered off and purified by crystallization from water; it separated from this solvent in small needles which melted with decomposition at 276°, though incipient fusion took place somewhat below this temperature. It is soluble in glacial acetic acid, alcohol and alkali, but insoluble in ether, benzene and acetone.

Anal. Calcd. for $C_{11}H_9O_3N_3$: N, 18.18; C, 57.14; H, 3.89. Found: N, 17.87; C, 57.36; H, 4.12.

B. Reduction with Hydriodic Acid in Glacial Acetic Acid.—Ten grams of hydantoin-($\Delta^{5,3'}$)-oxindole, 45 cc. of hydriodic acid (sp. gr. 1.7) and 100 cc. of glacial acetic acid were gently boiled in an oil-bath for forty-five minutes, or until complete solution was effected. After removal of the acids by distillation under diminished pressure, the residue was carefully extracted with boiling water and any solid material filtered off. On cooling the filtrate, the reduced hydantoin separated in characteristic needles, which were purified as in the previous method by crystallization from water. This substance melted unchanged (276°) when mixed with the product obtained by the reduction with tin and hydrochloric acid.

Anal. Calcd. for $C_{11}H_9O_3N_3$: N, 18.18. Found: N, 18.00.

2-Quinoline-4-carboxylic Acid. (IV.) A. By the Action of Barium Hydroxide on **Hydantoin-(5,3′)-oxindole.**—Ten grams of hydantoin-(5,3′)-oxindole, 75 g. of barium hydroxide, and 76 cc. of water were digested in an oil-bath under return condenser for two days, or until the evolution of ammonia had ceased. The reaction mixture was then diluted with 100 cc. of boiling water, the barium carbonate filtered off, thoroughly washed with water and the washings combined with the filtrate. Carbon dioxide was passed into the latter and, after boiling, a further quantity of barium was removed by filtration. By careful addition of dilute sulfuric acid to this hot filtrate, the remaining barium was completely precipitated as sulfate, which was immediately filtered off in order to avoid loss of the quinoline acid, which would have crystallized from the cool solution. The solution was then acidified strongly with acetic acid. Upon standing, it deposited silky needles of 2-quinolone-4-carboxylic acid. It was purified by three crystallizations from water. The yield was 2 g., or 25% of the theoretical.

The acid is soluble in alkali (from which it is precipitated by acid), and in hot water, but practically insoluble in cold water, absolute alcohol or benzene. It does not melt below 300".

Anal. Calcd. for $C_{10}H_7O_3N$: C, 63.49; H, 3.70; N, 7.41. Pound: C, 62.95; H, 3.79; N, 7.45.

B. By the Action of Sodium Hydroxide on Acetyl-isatin.—Five grams of acetylisatin dissolved in a 10% sodium hydroxide solution was heated for one hour on the steam-bath. On cooling and acidifying, the product separated, contaminated with some isatin. It was purified by crystallization from water after decolorization with Norite; yield, 3 g.

C. By the Action of Malonic Acid on Isatin.—Eight grams of malonic acid, 10 g. of isatin and 15 g. of glacial acetic acid were heated on the steam-bath for ten hours. The reaction mixture was poured into water; the impure acid was filtered off, triturated with alcohol to remove isatin and finally crystallized from water in which some Norite was used for decolorization purposes; yield, 8 g.

Methods. B and C except for some changes in methods of procedure were based on those of Camps6 and of Borsche and Jacobs,[6] respectively. The acid produced by either method was identical with that resulting from method A, and the ethyl ester (m. p. 205°) in either case was identical with that prepared from A.

2-Keto-1,2,3,4-tetrahydroquinoline-4-carboxylic Acid. (V.) A. By the Action of Hydriodic Acid on **Hydantoin-($\Delta^{5,3'}$)-oxindole.**—Ten grams of hydantoin-oxindole, 6 g. of red phosphorus and 60 cc. of hydriodic acid (sp. gr. 1.7) were heated for seven hours at 150°. The excess hydriodic acid was then removed by distillation under diminished pressure, the residue digested with hot water and the phosphorus filtered off. The tetrahydro acid crystallized from the filtrate upon cooling. It was purified by crystallization from hot water. It separates from this solution in characteristic colorless needles which melt at 217–218". The yield was 4.5 g., or 54% of the theoretical. It is soluble in hot water and alcohol and slightly soluble in benzene. It dissolves in sodium hydroxide solutions, from which it is reprecipitated unchanged on acidification with strong acids.

Anal. Calcd. for $C_{10}H_9O_3N$: N, 7.33; C, 62.83; H, 4.71. Found: N, 7.20; C, 62.11; H, 4.54.

B. By the Action of Hydriodic Acid on **2,5-Diketopiperazine-($\Delta^{3,6,3',3'}$)-di-(oxindole).**—Two and five-tenths grams of 2,5-diketopiperazine-($\Delta^{3,6,3',3'}$)-di-(oxindole), 1.8 g. of red phosphorus, and 17 cc. of hydriodic acid (sp. gr. 1.7) were heated for seven hours at 150°. It was then isolated from the reaction mixture by the same procedure that was employed in the preceding experiment. The yield was 35% of the theoretical.

Anal. Calcd. for $C_{10}H_9O_3N$: N, 7.33. Found: N, 7.55, 7.45.

C. By the Action of Hydriodic Acid on **Hydantoin-($\Delta^{5,3'}$)-5,7-dibromo-oxindole.**—The tetrahydro acid was prepared from this condensation product in a manner similar to A; yield, 40% of the theoretical. The isatin nuclei were completely debrominated in this experiment.

D. By the Action of Hydriodic Acid on **2-Quinolone-4-carboxylic** Acid.—One and one-half g. of 2-quinolone-4-carboxylic acid, 10 cc. of hydriodic acid and one gram of red phosphorus were heated in an oil-bath at 140" for five hours. After removal of the hydriodic acid by distillation under diminished pressure, the quinolone-carboxylic acid was extracted from the residue with hot water and purified as above; yield, 1 g.

The acid resulting from this method was identical with that produced by Methods A, B and C, respectively, and with Granacher"s[3] so-called oxindole-acetic acid, which was prepared by us precisely in accordance with his directions. The ethyl esters prepared by the esterification of the acids derived from any of these sources were identical; m. p. 155°.

The Ethyl Ester of **2-Keto-1,2,3,4-tetrahydroquinoline-4-carboxylic** Acid. (VI.) The Action of Tin and Alcoholic Hydrogen Chloride on **2-Quinoline-4-carboxylic** Acid.—Five grams of the unsaturated acid and 20 g. of mossy tin in 200 cc. of absolute alcohol were heated on the steam-bath for eight to ten hours, while hydrogen chloride was intermittently passed through the mixture. The unchanged tin was then filtered off and the greater part of the alcohol removed by distillation under diminished pressure. The residue was then poured into water slightly acidified with hydrochloric acid, and the ester separated as a white solid which was purified by crystallization from 50% alcohol. It crystallized in characteristic colorless needles which melted at 155". It is soluble in water and alcohol, but insoluble in dilute alkali. The same ester was prepared by the direct esterification of the acid derived from each of the various methods given above for the synthesis of 2-keto-tetrahydroquinoline-4-carboxylic acid.

Anal. Calcd. for $C_{12}H_{13}O_3N$: N, 6.39. Found: N, 6.57, 6.61.

Condensation Products of Hydantoin with 5-Bromo-isatin and **5,7-Dibromo-isatin.** General Procedure.—Five grams of hydantoin, 11.3 g. of monobromo-isatin (or 15.2 g.

of dibromo-isatin), 10 g. of fused sodium acetate, 50 cc. of glacial acetic acid and five drops of acetic anhydride were heated for four hours in an oil-bath at 150". The solids dissolved upon application of heat and the condensation products separated soon after. In each case the reaction mixture was poured into water and the precipitate triturated several times with hot water, filtered off and dried at 100°. Because of the insolubility of these indigoids in all common solvents, their soluble impurities were removed by successive digestions with acetic acid, water and alcohol. The monobromo condensation product is red in color and the dibromo derivative is orange. The yield in the case of the former was 30%; in the case of the latter, 88%. Neither indigoid melted below 300°.

Anal. (Hydantoin-($\Delta^{5,3'}$)-5′-bromo-oxindole). Calcd. for $C_{11}H_6O_3N_3Br$: N, 13.63; Br, 25.97. Found: N, 13.85; Br, 26.43.

Anal. (Hydantoin-($\Delta^{5,3'}$)-5′,7′-dibromo-oxindole). Calcd. for $C_{11}H_5O_3N_3Br_2$: N, 10.85; Br, 41.34. Found: N, 10.77; Br, 41.60.

Condensation Products of Diketopiperazine with Isatin, 5-Bromo-isatin and 5,7-Dibromo-isatin **2,5-Diketopiperazine-($\Delta^{3,6,3',3'}$)-di-(oxindole). (VIII.)**—Thirteen grams of isatin, 5 g. of diketopiperazine, 25 g. of anhydrous sodium acetate and 50 cc. of acetic anhydride were heated at 120–130° for five hours. Complete solution occurred immediately on heating this mixture, but this was followed shortly by voluminous precipitation of the condensation product. The mixture was finally poured into water and 16 *g.* of the impure indigoid obtained by filtration. It was purified by digesting it successively with glacial acetic acid, water and alcohol. The yield was 4.7 g., or 28% of the theoretical. This red condensation product is insoluble in all the common solvents. It dissolves, however, in concd. sulfuric acid, to which it imparts a deep permanganate color. It does not melt below 300°. As would be expected, both isatin nuclei were acetylated in this condensation.

Anal. Calcd. for $C_{20}H_{12}O_4N_4$: N, 12.28; C, 63.15; H, 3.51. Found: N, 12.23; C, 62.79; H, 3.87.

Except for the addition of an amount of fused sodium acetate roughly equivalent to the weight of the isatin derivative used, 5-bromo-isatin and 5,7-dibromo-isatin were condensed with diketopiperazine in similar fashion to the above. The condensation products were even less soluble than the indigoid derived from isatin. They could be superficially purified only by successive treatments with glacial acetic acid, water and alcohol, with a view to removing soluble impurities. The yields were not good. Both compounds are reddish-brown in color, and do not melt below 300°.

Anal. (2,5-Diketopiperazine-($\Delta^{3,6,3',3'}$)-di-(5′-bromo-oxindole)). Calcd. for $C_{24}H_{14}O_6N_4Br_2$: N, 9.12; Br, 26.00. Found: N, 8.4; Br, 25.23.

Anal. (2,5-Diketopiperazine-($\Delta^{3,6,3',3'}$)-di-(5′,7′-dibromo-oxindole)). Calcd. for $C_{24}H_{12}O_6N_4Br_4$: N, 7.25; Br, 41.44. Found: N, 7.65; Br, 42.63.

Summary

1. The indigoid hydantoin-($\Delta^{5,3'}$)-oxindole can be converted into hydantoin-(5,3′)-oxindole by the action of tin and alcoholic hydrogen chloride, or by hydriodic acid.

2. The hydrolysis of hydantoin-(5,3′)-oxindole with barium hydroxide yields 2-yuinolone-4-carboxylic acid, while hydrolysis with hydriodic acid, in the presence of phosphorus, yields 2-keto-1,2,3,4-tetrahydroquinoline-4-carboxylic acid.

3. 2-Keto-tetrahydroquinoline-4-carboxylic acid may also be prepared

by the direct action of hydriodic acid and phosphorus upon the following: 2-quinolone-4-carboxylic acid; hydantoin-($\Delta^{5,3'}$)-oxindole; hydantoin-($\Delta^{5,3'}$)-5',7'-dibromoxindole and 2,5-diketopiperazine-($\Delta^{3,6,3',3'}$)-di-(oxindole). The ethyl ester of the acid is formed by the action of tin and alcoholic hydrogen chloride on 2-quinolone-4-carboxylic acid.

4. 5-Bromo-isatin, and 5,7-dibromo-isatin will condense with hydantoin and also with diketopiperazine.

NEW HAVEN, CONNECTICUT

[A CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, UNIVERSITY OF WISCONSIN, AND THE OFFICE OF CEREAL CROPS AND DISEASES, BUREAU OF PLANT INDUSTRY]

A METHOD FOR THE DETERMINATION OF URONIC ACIDS[1]

BY ALLAN D. DICKSON, HENRY OTTERSON AND KARL PAUL LINK

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Introduction

During the course of numerous investigations on the composition of the cell wall of various plants we have had occasion to devote considerable time to the chemistry of the acid polysaccharide constituents. These acidic polysaccharide substances are uronic acids or polymerized anhydride derivatives of such acids. In the past twenty years these substances have attracted considerable attention from numerous investigators, not only because of their almost universal occurrence in the plant world but also because these substances without question play an important role in the carbohydrate metabolism of the cell and also serve as structural components of the cell wall.[2]

An aldobionic acid, glucoso-glucuronic, has been shown by Heidelberger and Goebel to be the fundamental building stone of the polysaccharide derived from Type III pneumococcus and to be an important constituent

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[1] Published with the permission of the Director of the Wisconsin Agricultural Experiment Station.

[2] Tollens, *Ber.*, 41, 1788 (1908); Ehrlich, *Chem.-Ztg.*, 41, 197 (1917); *Z. angew. Chem.*, 40, 1305 (1927); *Biochem. Z.*, 168, 263 (1926); *ibid.*, 169, 13 (1926); *ibid.*, 203, 343 (1928); Nanji, Paton and Ling, *J. Soc. Chem. Ind.*, **44**, **253T** (1925); Schmidt and co-workers, *Ber.*, 58, 1394 (1925); *ibid.*, 59, 1585 (1926); *ibid.*, 60, 503 (1927); also *Zeitschrift "Der Papier Fabrikant"*, 26 Jahrgang, Heft 28, 1–7 (1928); Schwalbe, *Ber.*, 58, 1534 (1925); Marcusson, *Z. angew. Chem.*, **39**, 898 (1926); Schryver and Norris, *Biochem. J.*, 19, 676 (1925); O'Dwyer, *ibid.*, 20, 657 (1926); *ibid.*, 22, 381 (1928); Hagglund and co-workers, *Z. physiol. Chem.*, 177, 248 (1928); Cretcher and Nelson, *Science*, 67, 537 (1925); Cretcher and Butler, *ibid.*, 68, 116 (1928); Candlin and Schryver, *Proc. Roy. Sor., London*, **103B**, 365 (1928); Henderson, *J. Chem. Soc.*, 2117 (1928); Szent-Gyorgyi, *Biochem.* J., 22, 1387 (1928); Rehorst, *Ber.*, 62, 519 (1929); Ehrlich and Rehorst, *ibid.*, 62, 628 (1929); Weinmann, *ibid.*, 62, 1637 (1929); Norris, *Biochem. J.*, 23, 195 (1929); Butler and Cretcher, THIS JOURNAL, 51, 1519 (1929); Norman, *Biochem.* **J.**, 23, 524 (1929).

in the pneumococcus from Friedlander's bacillus.[3] In our extensive studies on the composition of corn (*Zea* Mays) seedlings we have found that free glucuronic acid is present within the cell, that a polymerized glucuronic acid comprises part of the pectinaceous substances of the cell and cell wall, and that glucuronic acid is also intimately associated with the cellulose of the cell wall.[4]

Methods for the Determination of **Uronic** Acids.—Recently several methods have been devised for the determination of uronic acids and polyuronic acid substances.[5] These methods are all based on the original determination of Lefèvre and Tollens.[6] Their work showed that when glucuronic acid (anhydride or lactone) is heated with hydrochloric acid sp. gr. 1.06, under conditions similar to those employed for determining pentoses, it is decomposed according to the following equation

$$C_6H_{10}O_7 = C_5H_4O_2 + CO_2 + 3H_2O$$

The yield of furfural is less than the theoretical, whilst that of carbon dioxide is practically quantitative (22.70% of the uronic acid). Since the details of the apparatus and method used by Dore and McKinnis were never published in full and in view of the fact that the method that we have devised is more convenient and more expedient than the method of Nanji, Paton and Ling,[5] we thought it advisable to publish, in detail, the method that we have employed in our researches the past three years.

There are several important factors that Lefèvre and Tollens did not stress sufficiently in the description of their method. To insure complete decarboxylation of uronic acids or polymerized uronic acid substances by heating in 12% hydrochloric acid, it is necessary to conduct the decarboxylation at a bath temperature of 135–140° for at least four hours, preferably five.

The method described below has been used with uniform success on pure crystalline uronic acids, uronic acid lactones and polyuronic acids isolated from citrus pectin and from the cell wall of several plant tissues. The method gives equally satisfactory results on extracts or solutions that contain the afore-mentioned compounds in the presence of organic acids, sugars and polysaccharide substances. We have found that the quantity of carbon dioxide liberated by the action of 12% hydrochloric acid on various plant acids, both hydroxy and dicarboxylic, the sugars and sugar acids and many polysaccharides is very small. In a forthcoming paper we shall publish these results in full along with other data which will

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[3] Heidelberger and Goebel, *J. Biol. Chem.*, 70, 613 (1926); *ibid.*, 74, 613 (1927).

[4] Forthcoming paper; see also Link, THIS JOURNAL, 51,2506 (1929).

[5] Nanji, Paton and Ling, *J. Soc. Chem. Ind.*, *44*, 253T (1925); Dore, THIS JOURNAL, 48,232 (1926); McKinnis, *ibid.*, 50, 1911 (1928).

[6] Lefèvre and Tollens, *Ber.*, 25,2569 (1892); *ibid.*, 40,4153 (1907).

demonstrate the value of the determination of uronic acid in plant physiological and plant chemical studies.

Description of Apparatus Used.—The apparatus consists essentially of a 500-cc. reaction flask C connected by a ground glass joint to an Allihn 25-cm. reflux condenser D, which in turn is connected to a Truog[7] absorption tower F, through a trap E containing 10% silver nitrate to remove any hydrochloric acid gas that might pass the condenser. Two 20-cm. soda lime towers A, and a bulb water trap B are placed ahead of the reaction flask to remove the carbon dioxide from the air aspirated through the system.

The reaction flask is equipped with a side-arm tube that extends below the neck, to facilitate the removal of the liberated carbon dioxide by the air slowly drawn through the apparatus. The absorbing tower F is connected to a water pump through a safety bottle H of 4-liter capacity. A screw cock, 2, on the rubber tube connection between the tower and safety bottle is used to regulate the rate of aspiration. Heat is applied to the reaction flask by means of an oil-bath heated with an electric hot-plate. All connections are made with heavy walled rubber tubing. The accompanying figure illustrates the details of the apparatus.[8]

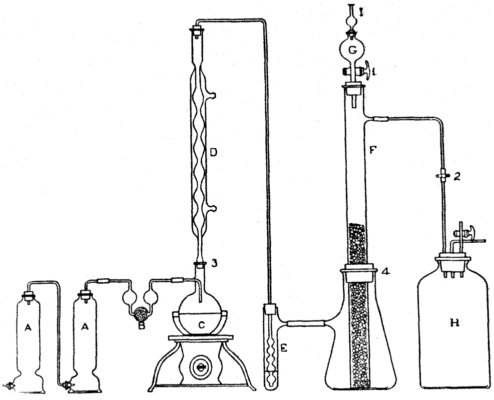

Fig. 1.—Apparatus for the determination of uronic acids.

Analytical Procedure.—The sample (0.2–0.5 g. of uronic acid) or substance to be analyzed is placed in the reaction flask C with 100 cc. of 12% hydrochloric acid (sp. gr. 1.06). A few boiling chips are added to prevent bumping. In dealing with solutions or liquid extracts enough concentrated hydrochloric acid is added to make the concentration equivalent to a 12% solution. The ground glass joint **3** is greased with vacuum stopcock grease to insure an air-tight joint and to prevent the joint from sticking.

The absorbing tower is assembled, filled about two-thirds full with dry glass beads, and connected with the silver nitrate trap E and the safety bottle. The rubber stopper joint 4 between the head tower and the suction flask can be sealed with paraffin to insure an absolutely tight connection. After the dropping funnel G is charged with a measured amount of $N/5$ barium hydroxide solution and put in place at the top of the tower a slow current of carbon dioxide-free air is drawn through the apparatus for fifteen to twenty minutes to remove the air in the system. The dropping funnel G is equipped with a small soda lime tube I. Heat is then applied to the reaction flask. Just as the solution in the flask begins to boil, the barium hydroxide solution is slowly introduced into the tower and washed down with several successive small portions of carbon dioxide-free distilled water. As the solution in the reaction flask C reaches the

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[7] Truog, J. Ind. Eng. *Chem.*, 7, 1045 (1915).

[8] In the method used by Dore the liberated carbon dioxide is collected in potash bulbs. McKinnis used a scrubbing tower (type not described) containing barium hydroxide. As mentioned in the text these authors did not publish the details of the apparatus and procedure used. Nanji, Paton and Ling use several absorption cylinders containing $N/10$ barium hydroxide to collect the liberated carbon dioxide and make use of a gas holder containing air freed from carbon dioxide to sweep out the apparatus.

boiling point and at the moment the barium hydroxide solution is introduced into the tower the air current must be increased sufficiently to prevent the expanding vapors in the reaction flask from passing over into the water trap B and soda lime tower A. The air current is then adjusted so that two to three bubbles per second pass through the tower. The temperature of the oil-bath should be maintained at about 135–140°. After the rate of aspiration and the temperature have been regulated the apparatus requires only intermittent attention. At the end of four to five hours the heating is discontinued and the aspiration is stopped by closing the screw cock *2*. The tower is disconnected from the trap E and the stopcock 1 is opened to allow the barium hydroxide solution to flow down into the flask, after which it is again closed. The rubber tube connection is removed from the side arm of the tower, the dropping funnel is taken off and the entire contents of the tower are washed down into the flask with carbon dioxide-free distilled water.

The excess barium hydroxide is titrated with $N/10$ hydrochloric acid, using phenolphthalein as the indicator. Thymolphthalein can also be used with equal success. After the titration is completed, the tower and beads are washed with dilute hydrochloric acid to remove the barium carbonate, washed free from acid and dried in an oven. It is important to remove the condenser from the flask while the flask is still hot to prevent the ground glass joint from sticking. When the samples or solutions to be analyzed for uronic acid contain free carbonates, it is necessary to boil the solution with dilute hydrochloric acid (below *2%)* to decompose the carbonate before making the decarboxylation analyses.

Calculation of Results.—One cc. of $N/5$ barium hydroxide solution is equivalent to *0.0044* g. of carbon dioxide. The blank determination on the 12% hydrochloric acid will correct for any carbon dioxide absorbed during the process of charging the apparatus and the titration. It will also detect the presence of minute leaks in the system. The blank determinations should never give titrations larger than *0.20* cc. of $N/10$ hydrochloric acid, which is less than the titration error with the same quantity of barium

SUMMARY OF ANALYTICAL RESULTS

Substance	Carbon dioxide, % Calcd.	Found	
Galacturonic acid, $C_6H_{10}O_7$, m. p. 159°, $[\alpha]_D$ +53 40°	22 *71*	*22.44*	*22.44*
Glucuronic acid, $C_6H_{10}O_7$, m. p. 156°, $[\alpha]_D$ +34.0	22 *71*	*22.54*	*22.57*
Glucuronic acid lactone, $C_6H_8O_6$, m. p. 175–176°, $[\alpha]_D$ +19.0°	*25.00*	*24.87*	*24.89*
Barium salt of galacturonic acid, $(C_6H_8O_7)_2Ba$, Ba, *26.85%*	*16 82*	*16.62*	*16.60*
Digalacturonic acid, $C_{12}H_{16}O_{12}$, $[\alpha]_D$ +240.80°	*24.70*	*24.45*	*24.45*
Purified lemon pectin	Equiv. to *72.60%* uronic acid anhydride[b]	*18.15"*	*18.11*
Citrus pectin[c]	Equiv. to *64.00%* uronic acid anhydride	*16.06*	*15.95*

[a] The percentage of carbon dioxide multiplied by 4 gives the percentage of uronic acid anhydride in a sample. The percentage of carbon dioxide multiplied by *5 66* gives the percentage of pectin material.

[b] The uronic acid anhydride values of highly purified pectin preparations vary from *70.00–73.00*% (Nanji, Paton and Ling, Ref. *5)*.

[c] Obtained from the California Fruit Growers Exchange Laboratory, Ontario, California.

hydroxide solution titrated directly. When the blank titration is 0.20 cc. of $N/10$ hydrochloric acid or less, this indicates that only 0.10 cc. of barium solution has been neutralized in the determination by carbon dioxide in the system and admitted in the process of charging the tower.

As an example of the calculation the analytical figures obtained on an authentic specimen of galacturonic acid are given: 0.20-g. samples were decarboxylated at 142° for five hours; 25.00 cc. of $N/5$ barium hydroxide solution was used in the absorption tower; 25.6 cc. of $N/10$ hydrochloric acid equivalent to 12 80 cc. of $N/5$ acid was consumed in the back titration, leaving an equivalent of 10.20 cc. of $N/5$ barium hydroxide neutralized by the liberated carbon dioxide. Multiplied by the factor 0.0044 this is equal to 0.04488 g. of carbon dioxide or 22.44% (theoretical 22.71%).

Addendum January 16, 1930

After the manuscript of the above communication had been sent to the Editor, an article by Ehrlich and Schubert [(*Ber.*, 62, 1974 (1929))] appeared, in which they discuss (page 2023) the determination of galacturonic acid in pectin substances. The analytical results obtained by our method are in agreement with those of Ehrlich and Schubert. That is, free galacturonic acid and polymerized galacturonic acid anhydride substances can be quantitatively determined by measuring the amount of carbon dioxide liberated by boiling with 12% hydrochloric acid. Ehrlich and Schubert use essentially the same apparatus that van der Haar devised as an improvement of the original of Tollens and Lefèvre Ref. 6. The analytical procedure is modified, however, by conducting the decarboxylation for a period of eight to ten hours instead of three and one-half to four hours. We agree that it is necessary to heat uronic acid substances in 12% hydrochloric acid longer than three and one-half to four hours to ensure complete decarboxylation. However, we have found that the decarboxylation of all the substances tried so far was complete within five hours when the temperature of the oil-bath that contains the reaction flask is maintained at 135–140°. The longer period of eight to ten hours which Ehrlich and Schubert found necessary for complete decarboxylation can possibly be attributed to the fact that the reaction temperature is lower under their conditions, as they do not state the temperature used. It is also possible that the volume of air swept through the apparatus to remove the liberated carbon dioxide is smaller than under our conditions, thus necessitating a longer period for the determination.

Summary

1. An apparatus and method, a modification of the Lefèvre–Tollens method, for the accurate determination of uronic acids by decarboxylation with hydrochloric acid (sp. gr. 1.06) is given.

2. The method is described in detail and the results obtained with authentic specimens of galacturonic acid, glucuronic acid and lactone, the barium salt of galacturonic acid, digalacturonic acid and several pectin preparations are given.

3. In all cases the results obtained approximate the theoretical values.

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MADISON, WISCONSIN

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

DIARSYLS. II. TETRA-ARYLDIARSYLS[1]

BY F. F. BLICKE, O. J. WEINKAUFF AND G. W. HARGREAVES

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Recently it was discovered[2] in this Laboratory that diarylarsyl iodides, dissolved in ether or benzene, react rapidly with mercury at ordinary temperature to form tetra-aryldiarsyls. Hitherto these compounds have been obtained by reduction of diarylarsinic acids or tetra-arylarsyl oxides with phosphorous acid in hot alcoholic[3] or acetic acid solution. Inasmuch as elevated temperatures, solvents and acids which may interact with the diarsyls are entirely eliminated, the first-mentioned method is especially adapted for the preparation of such extremely reactive compounds as the tetra-aryldiarsyls.

We prepared, previously, solutions of tetraphenyl-, tetra-*p*-tolyl-, tetra-p-anisyl-, tetranaphthyl and tetrabiphenyldiarsyl but only the phenyl compound was isolated in the solid state. With the exception of tetraphenyldiarsyl[4] none of the five compounds mentioned had ever been prepared.[5] We have isolated now, in the solid state, all of the diarsyls mentioned above with the exception of tetrabiphenyldiarsyl and, in addition, dibiphenylenediarsyl and 6,6-bisphenoxarsine.

The great interest in the tetra-aryldiarsyls lies in the question as to whether or not they undergo spontaneous dissociation in solution into diarylarsyls, that is, into divalent arsenic radicals, $R_2As—AsR_2 \rightleftharpoons 2R_2As—$. The extreme rapidity with which a solution of tetraphenyldiarsyl and other tetra-aryldiarsyls absorb an amount of oxygen which corresponds to the volume of this gas required for the formation of a peroxide and the great reactivity of the diarsyls toward other reagents indicates that solutions of these substances contain a very reactive arsenic compound,

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[1] This investigation was made possible by a grant from the Faculty Research Fund of the University of Michigan.

[2] Blicke and Smith, THIS JOURNAL, 51, 2272 (1929).

[3] Porter and Borgstrom [*ibid.*, 41, 2050 (1919)] showed that hot alcohol decomposes tetraphenyldiarsyl with the formation of diphenylarsine.

[4] LaCoste and Michaelis, *Ann.*, 201, 222 (1880); Michaelis and Schulte, Ber., 15, 1952 (1882); Michaelis, *Ann.*, 321, 148 (1902); Schlenk, *ibid.*, 394,216 (1912); Porter and Borgstrom, THIS JOURNAL, 41, 2048 (1919); Borgstrom and Dewar, *ibid.*, 44, 2915 (1922).

[5] Other investigators claim to have obtained in solid form the following aromatic tetra-aryldiarsyls but no special precautions seem to have been taken to prevent oxidation of the diarsyl during the isolation of the latter: tetra-3-nitrophenyl- [Michaelis, *Ann.*, 321,149 (1902)], tetra-3-aminophenyl- [French Patent, 440,128; Michaelis, *ibid.*, 321, 150 (1902)], tetra-3-acetylaminophenyl- [Michaelis, *ibid.*, 321, 150 (1902)], tetra-3-amino-4-hydroxyphenyldiarsyl [Fargher, *J. Chem. Soc.*, 115, 987 (1919)] and 6,6-bisphenoxarsine [Lewis, Lowry and Bergeim, THIS JOURNAL, 43, 894 (1921)]. None of these compounds have been studied in detail.

possibly one in which arsenic is in a divalent state. During this investigation we sought to obtain positive proof of a dissociation of tetra-aryldiarsyls through molecular weight determinations.

As a result of our investigation we can only say that in the event any of the five diarsyls tested undergo dissociation, under the conditions used in our experiments, the dissociation in no case exceeds 10%. Unfortunately, due to the magnitude of the errors inherent in our present methods for the determination of molecular weights, trustworthy evidence of dissociation cannot be obtained in the case of compounds which dissociate only to a comparatively slight extent.

A variety of other tetra-aryldiarsyls are being prepared in the hope that compounds may be found which will dissociate to such a degree that positive evidence of dissociation may be secured through molecular weight determinations.

Experimental Part

The preparation of diphenyl-, di-*p*-tolyl-, di-*p*-anisyl- and di-α-naphthylarsyl iodides has been described previously.[6]

Biphenylene-arsyl Iodide.—Biphenylene-arsyl chloride[7] was prepared in the following manner. Seventy-seven g. of diphenyl (0.5 mole), 135 g. of arsenic trichloride (0.75 mole) and 10 g. of aluminum chloride were placed in a flask fitted with a reflux condenser. The flask was heated in a metal-bath for about three and one-half hours, when the temperature of a thermometer which dipped into the mixture reached 165°. Ten g. more of aluminum chloride was added and the mixture heated for about an hour longer, when the temperature reached 185°. The reaction product was then boiled for about fifteen minutes with 250 cc. of benzene and a small quantity of hydrochloric acid. The benzene layer was separated, dried and after removal of most of the benzene the residue was distilled under diminished pressure. The material which boiled between 225–245° under 30-mm. pressure was collected. The yield of crude product was 27 g. After recrystallization from benzene the diphenylene-arsyl chloride melted at 161°. The chloride was dissolved in acetone and treated with one and one-half times the calculated amount of sodium iodide dissolved in the same solvent. After eight hours the mixture was decanted into an equal volume of water, whereupon the yellow iodide precipitated in crystalline form. The iodide was recrystallized from a mixture of benzene and petroleum ether; m. p. 166–167°.

Because of the great insolubility of the diarsyl we isolated only enough of this material for an oxygen absorption, a melting point determination and an analysis.

6-Iodophenoxarsine.—6-Chlorophenoxarsine was prepared by a method described by Pope.[8] The chloride was then converted into the iodide in the usual manner; the

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[6] Blicke and Smith, THIS JOURNAL, 51,1565 (1929).

[7] This compound has been obtained by Aeschlimann, Lees, McCleland and Nicklin [*J. Chem. Soc.*, 127, 66 (1925)] by the reduction of biphenylene-arsinic acid in the presence of hydrochloric acid; the iodide was described also. These investigators made an unsuccessful attempt to prepare the diarsyl by the reduction of the arsinic acid with zinc and hydrochloric acid.

[8] This method is mentioned in an article by Lewis, Lowry and Bergeim, THIS JOURNAL, 43, 892 (1921).

arsyl iodide melted at 145–146°. From p-bromodiphenyl ether,[9] arsenic trichloride and aluminum chloride we obtained a colorless, oily reaction product which, when treated with sodium iodide in acetone solution, yielded a yellow, crystalline product. The structure and properties of this substance will be discussed in a later paper.

Preparation and Isolation of the Diarsyls.—One hundredth mole of the diarylarsyl iodide was put into a three-ounce, narrow-necked bottle and enough dry benzene, which had been saturated previously with dry nitrogen, was added to almost fill the bottle. A stream of nitrogen was passed through the solution for a short time and after the addition of 12 g. of mercury the bottle was stoppered and shaken for ten hours. The solution was then filtered into a special apparatus.[10] The bulb of the apparatus was immersed in a water-bath, the temperature of which was about 70°, and the benzene was removed under diminished pressure.[11] The crystalline residue was washed three times with 10 cc. of oxygen-free, absolute ether and the ether removed through the upper outlet tube with the aid of suction. The solid material in the bulb of the apparatus was heated again in the water-bath (80–90°) under a pressure of 20 mm. for four hours.[12]

The diarsyls were obtained in the form of powders which did not adhere to the sides of the bulb. The apparatus was now put into a cylindrical can which was ten inches high and nine inches in diameter. In the bottom of the latter there had been placed several disks of solid carbon dioxide and a stream of the dry gas was passed into the can. The short tube at the bottom of the bulb was broken and the diarsyl transferred to a test-tube. The diarsyl was then pressed into pellets in a pill machine and each pellet, the average weight of which was about 0.2 g., was placed in a small weighed tube which was just large enough to contain it. All of the above operations were carried out in the can filled with carbon dioxide.

TABLE I

DATA ON COMPOUNDS

Diarsyl	M. p.,[a] °C.	% Absorp., N. T. P.	Formula	Arsenic, % Calcd.	Arsenic, % Found
Tetraphenyl	129–130	107	....		
Tetra-p-tolyl	165–167	105	$C_{28}H_{28}As_2$	29.18	29.23
Tetra-p-anisyl[b]	172–175	107	$C_{28}H_{28}O_4As_2$	25.94	25.74
Tetra-a-naphthyl[c]	249–252	173[d]	$C_{40}H_{28}As_2$	22.79	22.91
6,6-Bisphenoxarsine[e]	176–177	104	$C_{24}H_{16}O_2As_2$	30.61	30.63
o,o'-Dibiphenylenediarsyl	269–273	108	$C_{24}H_{16}As_2$	33.04	33.20

[a] All melting-point determinations were made in sealed tubes filled with nitrogen.

[b] Because of the insolubility of this diarsyl there was used three times the amount of benzene necessary for the preparation of the phenyl analog.

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[9] Suter, THIS JOURNAL, 51, 2585 (1929).

[10] Gomberg and Schoepfle, *ibid.*, **39**, 1659 (1917). We modified this apparatus to the extent that the lower stopcock was removed.

[11] At this point the contents of one or two more bottles were siphoned into the apparatus so that 4-5 g. of the diarsyl could be isolated. In one instance we attempted to isolate a much larger quantity of the diarsyl but it was found that the compound retained benzene so tenaciously that the last traces of the solvent could not be eliminated completely by heating the bulb of the apparatus in a water-bath.

[12] In one instance tetraphenyldiarsyl, after it had been washed with ether and dried for a short time with the aid of suction, was placed in a test-tube and dried in a vacuum drying apparatus at 80° under 20-mm. pressure for four hours; 5.1090 g. of the material lost 0.0183 *g.* in weight. The material was heated for an hour longer but the loss in weight was negligible. The diarsyl seems to be oxidized much more readily when it contains traces of benzene than when it is thoroughly dry.

[c] Prepared from 3.42 g. of di-a-naphthylarsyl iodide, 9 g. of mercury and 90 cc. of bromobenzene.

[d] An absorption considerably over 100% is characteristic for tetra-α-naphthyldiarsyl and for tetrabiphenyldiarsyl.[2] The oxidation of the diarsyls proceeds in two stages. The first stage is the extremely rapid addition of one molecular equivalent of oxygen with the formation of a substance which may be a peroxide. The second stage of oxidation takes place much more slowly and, if moisture is present, the final oxidation products are the tetra-arylarsyl oxide and the diarylarsinic acid. The high absorption obtained immediately upon exposure of tetranaphthyldiarsyl to oxygen might be accounted for, *a priori,* in one of two ways: tetranaphthyldiarsyl decomposes, spontaneously, to a considerable extent in solution into products which absorb more oxygen than the parent substance; such an assumption, however, is disproved by the fact that pure tetranaphthyldiarsyl is obtained in good yield from a solution of the diarsyl upon removal of the solvent. The second stage of oxidation in the case of this substance proceeds with a much greater velocity than is ordinarily the case; at present we are inclined to favor this latter assumption.

[e] Lewis, Lowry and Bergeim, Ref. 5, prepared this substance by reduction of 6-phenoxarsine oxide with phosphorous acid in hot alcoholic solution. It was described as a yellow compound which melted at 159° and oxidized in air to a mixture of phenoxarsinic acid and 6-phenoxarsine oxide.

Molecular Weight Determinations

Procedure.—The Menzies[13] apparatus was used for all boiling point determinations. The apparatus was filled with dry, oxygen-free nitrogen. A short inverted test-tube to which a side arm had been attached was placed over the top of the apparatus and held in position by means of a thin ring of cork. A continuous stream of nitrogen was then passed through the side arm of the test-tube and escaped through a slit in the cork.

For freezing-point determinations the Beckmann apparatus was used and the solutions were agitated by means of a platinum stirrer which was operated by an electromagnet. The solvents used were saturated with nitrogen prior to the molecular weight determinations and a continuous stream of the gas was led through the top of the apparatus.

Before each series of molecular weight determinations the purity and activity of the diarsyl was established by means of melting point and oxygen absorption.

In some instances we demonstrated that the diarsyl had lost little or no activity during the molecular weight determinations. After the completion of a series of determinations in diphenyl the solution was allowed to solidify. The Beckmann tube, which contained the material, was closed with a stopper through which a dropping funnel and an outlet tube had been inserted and was then attached to the absorption apparatus in place of the ordinary absorption bottle. The whole apparatus was

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[13] Menzies, THIS JOURNAL, 43, 2309 (1921); Nenzies and Wright, *ibid.*, 43, 2314 (1921).

filled with oxygen[14] and then 50 cc. of bromobenzene was introduced into the Beckmann tube through the dropping funnel. After the solid material had all dissolved and the absorption of oxygen had ceased, 50 cc.[15] was added to the amount of absorbed gas and the volume was calculated for normal temperature and pressure. Since a mixture of bromobenzene and diphenyl had served as a solvent for the diarsyl, a mixture of these two substances was used in the gas buret instead of pure bromobenzene.

Titration with iodine to determine the amount of diarsyl present in solution may give very unreliable results since one of the oxidation prod-

TABLE II

MOLECULAR WEIGHT DETERMINATIONS~

	Diarsyl	Concn.. %	AT, °C.	Mol. wt., Found	Mol. wt., Calcd.
1	Tetraphenyl	**0.91**	**0.0520**	**455**	**458**
		1.63	.0933	456	
	M. p. 129–130°	**2.51**	.1452	**452**	
	Solvent **29.3** cc. A,' Eb.[c]	**3.39**	.1940	**456**	
Av. of **21** detns. on **4** different samples				455	
2	Tetraphenyl	**0.98**	.185	**419**	
	M. p. 129–130°	**2.07**	.379	**434**	
	Solvent **20.0** g. C[b], Cry.[c]	**3.18**	.591	**430**	
Av. of *7* detns. on **2** different samples				432	
3	Tetraphenyl, B,[b] **Eb.**			432[d]	**458**
4	Tetraphenyl, D,[b] Cry.			**429**	**458**
5	Tetra-*p*-tolyl, A, Eb.			**515**	**514**
6	Tetra-p-tolyl, C, Cry.			467	**514**
7	Tetra-*p*-anisyl, A, Eb.			**583**	**582**
8	Tetra-*p*-anisyl, C, Cry.			**551**	**582**
9	Tetra-a-naphthyl, **A,** Eb.			667	658
10	Tetra-a-naphthyl, C, Cry.			**615**	**658**
11	6,6-*Bis*-phenoxarsine, **A,** Eb.			506	**490**
12	6,6-*Bis*-phenoxarsine, C, Cry.			**460**	**490**

[a] In order to conserve space, complete experimental data has been given for only two series of determinations.

[b] A represents benzene, B ethyl acetate, C diphenyl and D naphthalene.

[c] Eb.—ebullioscopic method; Cry.—cryoscopic method.

[d] In this instance, as well as those which follow, the values recorded represent the average of **4** to **8** determinations on several different samples of material.

In those instances in which an oxygen absorption was carried out after the completion of the molecular weight determinations, the following results were obtained: Expt. 2, 102%; Expt. 6, 103%; Expt. 8, 103%; Expt. 10, 168%; Expt. **12, 109%.**

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[14] A possible refinement to the procedure would be the addition of a small quantity of paraffin, which had been warmed just enough to allow it to flow through the dropping funnel, to the Beckmann tube. The paraffin would congeal and protect the solid surface of the diarsyl solution from oxidation while the apparatus was being filled with oxygen.

[15] Due to a possible contraction in volume when the solvents were mixed, the volume of the gas displaced by the bromobenzene may have been slightly less than 50 cc.

ucts of the diarsyl—the tetra-aryldiarsyl oxide—also decolorizes, instantly, iodine dissolved in organic solvents.

Discussion of Results

Schlenk[16] obtained the value of 362 for the molecular weight of tetraphenyldiarsyl in boiling benzene; the calculated value is 458. Porter and Borgstrom[4] found 755 and 765 in naphthalene by the cryoscopic method. Borgstrom and Dewar[4] obtained an initial value of 686 in naphthalene but noticed a gradual increase in molecular weight as the solution of the diarsyl aged. Thus, after four hours, the molecular weight was found to be 766.

Our results differ materially from those of the last mentioned investigators. In boiling benzene we found that the molecular weight value remained perfectly constant for a period of two hours and in naphthalene there was no appreciable increase during a three-hour period of observation. Furthermore, the molecular weight of tetraphenyldiarsyl, determined in naphthalene, never exceeded the value 458.

It can be seen from the table that the average molecular weight values obtained in boiling benzene correspond on the whole quite well with the calculated values. However, the average molecular weights found in diphenyl are uniformly low. While we cannot state that these low values represent dissociation, it seems that the differences between the calculated molecular weights for the diarsyls and the molecular weights found are somewhat too large to represent experimental errors. If the results obtained with biphenyl as a solvent are calculated in terms of dissociation, it will be found that the amount of possible dissociation is from 6–10%.

Our procedures were tested for accuracy by molecular weight determinations of pure tetraphenylarsyl oxide. The calculated molecular weight of this substance is 474. In boiling benzene the average value of seven determinations was 472; in diphenyl, by the freezing-point method, the average value of three determinations was 467. All of these molecular weight determinations were carried out in a stream of dry, oxygen-free nitrogen.

All of the diarsyls which we isolated are colorless substances and yield colorless solutions when dissolved with the exception of 6,6-*bis*-phenoxarsine, which was yellow. Most of the crude diarsyls were somewhat yellow and tetra-*p*-anisyldiarsyl was distinctly yellow but the color was found to be due to the presence of an impurity which was removed when the diarsyl was washed with ether.

When protected from air and light the solid diarsyls are stable, at least over a period of several days.

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[16] Schlenk, *Ann,*. **394, 216** (1912).

Summary

A number of tetra-aryldiarsyls have been isolated in the solid state.

Molecular weight determinations have shown that in the event any of the diarsyls used in our experiments undergo dissociation, the magnitude of the dissociation, at 80°, does not exceed 10%.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

THE EFFECT OF HEAT UPON d-ALPHA-PINEME[1]

BY F. H. THURBER AND C. H. JOHNSON

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In the paper on Port Orford cedar wood oil by Thurber and Roll[2] the suggestion is made that since the pinene from the oil studied did not form a trace of the inactive nitroso chloride, it is probable that the product is a d-a-pinene isomeric with the ordinary form of d-a-pinene which is isolated from American turpentine oil. The purpose of this paper is to present some evidence in support of that suggestion.

Smith[3] determined the rate of racemization of d-a-pinene and calculated its heat of activation. He suggested that since α-pinene has two asymmetric carbon atoms "it would be expected that four isomeric modifications of the molecule, that is, two dextro and two levo forms, should exist." We would add that geometric isomers might also be expected because of the presence of the double bond. Many investigators have assumed that only two of these isomers, one dextro and one levo, are stable enough under ordinary conditions so that they may be isolated. However, a consideration of some of the common derivatives of α-pinene, such as the hydrochloride and the nitroso chloride, might lead one to a different conclusion. Thus we find that a-pinene nitroso chloride when prepared from highly optically active pinene is unstable in the air and is entirely different from the product prepared from inactive pinene. Also, pinene hydrochloride prepared from d-pinene is reported to be inactive, while that prepared from 1-pinene is reported to have a negative rotation, the numerical value varying with the activity of the pinene used in the preparation. Likewise, the constants, such as melting paints, reported in the literature for these compounds vary over a considerable range. It is clear that all of these differences which have been noted could be accounted for readily by assuming that the derivatives prepared, which show differences in properties, were made not from the same compound but from isomeric compounds. Rather than make such an assumption the differences noted are generally ascribed to differences in molecular aggregation or to degree of purity of the sample examined.

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[1] Revised paper; original received E'ebruary 23, 1928.

[2] Thurber and Roll, *Ind. Eng. Chem.*, 19,739 (1927).

[3] Smith, THIS JOURNAL, 49, 43 (1927).

The observations on inactive and levo pinene hydrochloride are more difficult to understand. If the dextro and levo α-pinenes were optical enantiomorphs one would expect their hydrochlorides to be identical. The best explanation at the present time of the above-mentioned observation is that pure l-α-pinene is difficult to prepare and, to the best of our knowledge, the hydrochloride of this pure product has never been prepared and studied.[4] We expect to take up such a study in a later paper.

We have tried for some time to find a laboratory method which would enable us to obtain further evidence regarding the existence of the theoretically possible α-pinenes. It occurred to us that the method Smith used for the determination of the heat of activation should lead to interesting results when applied to samples of pinene which presumably might have different structures. Molecules of different structure would differ in energy content, and thus the amount of heat required to activate them should be different, even though the molecules were closely related structurally.

For the reason stated above we decided to determine the heat of activation of pinene from Port Orford cedar wood oil and of pinene from turpentine oil. A number of samples of turpentine were examined but the rotation of most of them was rather low. A sample with an observed rotation of 63.4' in a 1-dc. tube was finally chosen. This was sufficiently high so that satisfactory readings after partial racemization could be made. Pinene from Port Orford cedar oil in a tube of the same length has an observed rotation of 125.4'. Later we expect to be able to compare l-pinene from Oregon balsam with these two d-pinenes, and with the one examined by Smith. It is also hoped that a satisfactory analytical method for determining differences in the structures of a-pinenes may be developed.

Experimental Part

The pinene from Port Orford cedar wood oil was obtained in the manner described in a previous article by one of us.[2] It was purified for immediate use by fractionation over metallic sodium. The fraction having a boiling point of 156–157° was used in this work. The pinene from turpentine was purified in the same manner and the boiling point range was the same.

The method of procedure was similar to that outlined by Smith.[3] The vapor, or vapor and liquid, of pinene was heated in a sealed tube for varying lengths of time at three different temperatures, namely, those of aniline, naphthalene and quinoline boiling freely under the atmospheric pressure prevailing during the course of an experiment. In order to drive the air from the reaction tubes without the use of highly efficient vacuum pumps and an absorption apparatus, an excess of the pinene was distilled from the tubes under a pressure of about fifteen millimeters. Since a practically constant boiling-point sample was used, this distillation should not affect

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[4] Lynn, THIS JOURNAL, 41, 361 (1919).

the composition of the sample remaining in the tubes. The tubes were sealed just before the liquid phase had disappeared. In making readings to note the change in optical activity, a polarimeter tube with a smaller diameter was used. Thus the volume of the liquid pinene condensing in the cold tube was sufficient so that it was not necessary to dilute the partially racemized product with a solvent to fill the polarimeter tube. The temperatures were corrected for variations from standard pressure by the usual formula for non-associated liquids. These corrections, per 10 mm. variation from standard pressure, amounted to 0.538° for aniline, 0.577° for naphthalene and 0.60" for quinoline.

The rate constants at each temperature were calculated according to the modified equation for *a* monomolecular reaction

$$K = \log_{10} (a_1/a_2) + (t_2 - t_1)0.8686$$

where a_1 is the polarimeter reading of original pinene, a_2 is the polarimeter reading of heated pinene and $t_2 - t_1$ is the length of the heating period in minutes. The results so calculated for both samples of pinene appear in Tables I and II.

TABLE I

PINENE FROM PORT ORFORD CEDAR OIL

Trial	Temp., °C.	Polarimeter readings	Time, minutes	10^5 K
A-1	184.2	37–33.2	2645	2.048
A-2	184.2	37–33.3	2830	1.862
A 3	183.9	37–33.6	2467	1.954
A 4	183 9	37–34.5	2475	1.413
A-5	184.6	37–32.7	2552	2.420
A-6	184 6	37–33.6	2746	1.755
A-7	184.2	37–34.5	2635	1.326
Av.	184.2	.....	..	1.825
N-1	217.8	37–14.9	917	49.590
N-2	217.8	37–24 9	424	46.700
N-3	217.3	37–23 8	457	48.272
N-4	217.5	37–26.1	350	49.853
N-5	218 3	37–25 8	310	58.150
N-6	218 2	37–28	290	48 052
N-7	217.8	37–33.6	153	31.498
N-8	217.6	37–29.1	256	46.908
Av.	217 8	.....	..	47.378
Q-1	236 7	37–24.6	80	255.1
Q-2	236.7	37–22.7	95	257.13
Q-3	236.7	37–24.5	84	245.38
Av.	236 7	.....	..	252.54

It is at once evident that corresponding rate constants, K, for the two pinenes are approximately 100% greater in the case of the pinene from turpentine. This would indicate either a different structure for the two compounds or the presence in one of them of some catalyzing impurity, or possibly both influences combined to give rise to so decided a difference in

TABLE II

PINENE FROM TURPENTINE OIL

Trial	Temp., °C.	Polarimeter readings	Time, minutes	$10^5 K$
A–1	184 8	63 4–52 7	2170	4.259
A–2	184 7	63 4-52	2359	4.2[illegible]2
A–3	184 4	63 4–53 3	2160	4.017
Av.	184 6			4.159
N–1	218 45	63 4–36 7	318	85.95
N–2	218 0	63 4–44 9	233	74.04
N–3	217 95	63 4–44 7	240	72.81
Av.	218 1	. . .		77.6
Q–1	236 7	63 4 4 1	62	351.5

the reaction rate. In this connection it was noted that in all of the determinations at higher temperatures, especially in boiling quinoline, the pinene from turpentine became yellow, and in some cases a brown, resin-like substance, only partially soluble in the reaction mixture, formed. The latter solutions were too brown to examine in the polarimeter.

The heat of activation of pinene would presumably vary with the structure and be approximately independent of catalytic influences, since the percentage change due to catalysis would be very nearly the same at different temperatures. It has already been pointed out by Smith that "the only objectionable impurities in the substance measured would be other optically active substances racemizing at nearly the same rate as that of the substance under investigation." The heat of activation was calculated according to the Arrhenius equation

$$Q = 2\ 303RT_1T_2 \log_{10} (K_2/K_1) + (T_2 - T_1)$$

where Q is heat of activation in calories, R is the gas constant in calories, K_1 is rate constant at the lower temperature, T_1 absolute, and. K_2 is rate constant at the higher temperature, T_2 absolute. The results so calculated for both samples of pinene appear in Tables III and IV.

TABLE III

PINENE FROM PORT ORFORD CEDAR OIL

Trials		Rate const., A	Rate const., N	Rate const., Q	Heat of act.
$A_{1,2}$	$N_{1,2}$	1.955	48.0885	....	42,570
$A_{1,2}$	$N_{3,4}$	1.955	49.0675		43,320
$A_{3,4}$	$N_{1,2}$	1.6835	48.0885		44,135
$A_{3,4}$	$N_{3,4}$	1.6835	49.0675	....	44,895
$A_{1,2}$	$Q_{1,2,3}$	1.955	.....	252.54	42,947
$A_{3,4}$	$Q_{1,2,3}$	1.6835	.....	252.54	43,986
$N_{1,2}$	$Q_{1,2,3}$	....	48.0885	252.54	43,691
$N_{3,4}$	$Q_{1,2,3}$	....	49.0675	252.54	42.231
Best value of K					43,472
A (av.)	N (av.)	1.825	47.378	....	43,286
N (av.)	Q (av.)	....	47.378	252.54	44,083
A (av.)	Q (av.)	1.825	.....	252.54	42,865
Average of all values obtained					43,411

TABLE IV

PINENE FROM TURPENTINE OIL

Trials	Rate const., A	Rate const., N	Rate const., Q	Heat of act.
A_1 N_1	4.259	85.95	...	39,977
A_1 N_2	4.259	74.04	...	38,478
A_2 N_1	4.2015	85.95	...	40,040
A_2 N_2	4.2015	74.04	...	38,543
A_3 N_3	4.017	72.81	...	38,600
Best value of K				39,128
A (av.) N (av.)	4.159	77.6	...	39,072
N (av.) Q_1	....	77.6	351.5	40,465
A (av.) Q_1	4.159	...	351.5	39,535
Average of all values obtained				39,691

The letters and subscripts in these tables refer to the trial numbers in Table I.

Conclusions

Although the difference in the heat of activation of these two samples of pinene is not very great, it is beyond the limits of experimental error occurring in this work. The best value of the heat of activation for pinene from cedar wood oil is approximately 4300 calories higher than the corresponding value for pinene from turpentine oil. When all determinations are taken into account, the average difference between the heats of activation of the two pinenes is about 3700 calories. Thus one may feel justified in concluding that these two samples have different structures. Any difference in optical properties, providing the molecular structures of the two samples were the same, should not influence in any way the heat of activation, since dextro and levo forms of the same molecule have identical structures and, therefore, the same energy content.

Although we do not know the source of the pinene which Smith used,[3] it evidently had the same structure as that of the pinene from Port Orford cedar oil, since the heats of activation of the two are approximately the same. The sample of pinene from turpentine appears to be a less stable isomer. It not only decomposes more readily, but its heat of activation is less than that of pinene from cedar oil.

It occurred to us that some interesting results should be obtained from a study of the nitroso chloride reaction of a sample of pinene before and after partial racemization. If it is only the high degree of optical activity that prevents the formation of a solid nitroso chloride, then after partial racemization there should be no difficulty in securing this nitroso chloride. On the other hand, if the two pinenes have different structures, and the ease of formation of the nitroso chloride depends only on the structure, then there should be no difference in the amount of this compound formed before and after racemization of the pinene.

To test the validity of this idea, a sample of the pinene from Port Orford cedar oil was heated to 200° in a closed evacuated tube for twenty-four hours. Ten cubic centimeters of the product was allowed to react with an equal volume of amyl nitrite in 10 cc. of glacial acetic acid. Upon the addition of hydrochloric acid a solid precipitated out which had the characteristic melting point (112°) of pinene nitroso chloride. This result was unexpected. However, it was found on fractionation of the remainder of the heated pinene that only a small portion had the boiling point of the original pinene. Some change aside from racemization had evidently occurred during the heating process. The formation of the nitroso chloride in this instance, therefore, had no significance from the point of view of proving or disproving the question of the existence of isomeric a-pinene.

Because of this observed increase in boiling point of the heated pinene, it would appear possible that the measured rates of reaction may have been determined by some reaction other than simple racemization. To test this point further we combined corresponding portions of the partially racemized pinenes, fractionated them and examined the several fractions in the polarimeter. The results appear in Table V.

TABLE V

RESULTS OF FRACTIONATION EXPERIMENTS

	Volumes, cc.	Boiling range, °C.	Rotations
Port Orford cedar oil heated by boiling aniline	1	Below 155	..
	12	155–158	36.9
	3	158–169	33.9
	3	169–185	26.8
	3	Above 185	Gummy residue
Port Orford cedar oil heated by boiling naphthalene	1	Below 155	
	5	155–158	33.0–34.0
	5	158–169	30.1
	5	169–185	22.0
	3	Above 185	Gummy residue
Turpentine oil heated by boiling aniline	1	Below 155	
	5	155–158	19.6
	5	158–169	17.5
	2.5	169–185	
	2	Above 185	Gummy residue

It will be noted that the greater portion of each sample distilled above 159°, indicating the presence of new compounds other than racemic pinene. However, the fraction which most nearly approximates the boiling point of pure pinene has a rotation approximating that of the original unheated pinene. The rotations given are the observed ones in all cases. The corresponding values for unheated pinene are 37 for the cedar oil, and 18.7 for the turpentine oil. It seems likely that a more thorough fractionation of a larger sample of the heated pinene would have given a pinene fraction with the same rotation as that of the unheated portion. We were unable to make this fractionation because of the small amount of material available. The observed rotation of the heated pinene samples is the average of the rotations of the several fractions appearing in the table.

It would seem, then, that the value which we have been measuring is the rate of rearrangement of pinene to other compounds, rather than the rate of racemization only. Smith[3] also must have been measuring the same value. Smith's interpretation of his results would then not be correct unless the decomposition was preceded by racemization, and the latter was the slower reaction.

In any event the results show that the two pinenes which we have examined are different, and that the one from Port Orford cedar oil is evidently similar in structure to that studied by Smith.

Summary

The rates of decrease in optical activity at three different temperatures of pinene from Port Orford cedar oil and of pinene from turpentine have been determined. The rate constant for the latter is practically twice as great as for the former.

Assuming the decrease in optical activity to be due to racemization, the heats of activation of these two pinenes have been calculated. The value obtained for pinene from turpentine is approximately 3700 calories less than that for pinene from cedar oil.

It is suggested that only a difference in structure between the two pinenes could explain all of the experimental results reported. Differences in structure of α-pinene molecules would account for at least part of the peculiar and conflicting reactions of a-pinene which have been observed and reported.

When d-α-pinene is heated *in vacuo* the major portion is converted to compounds with higher boiling points than the original pinene.

The rate of reaction measured may be either the rate of racemization or the rate of rearrangement, depending upon which reaction is the slower.

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[166TH CONTRIBUTION FROM THE COLOR AND FARM WASTE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

THE CHEMISTRY OF LIGNIN. IV. LIGNIN FROM OAT HULLS

BY MAX PHILLIPS

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Several investigators have reported on the composition of lignin obtained from annual crop plants. Beckmann, Liesche and Lehmann[1] investigated a lignin fraction isolated from winter rye straw and concluded that the composition of the lignin from that source may be represented either by the formula $C_{40}H_{44}O_{15}$ or $C_{42}H_{46}O_{16}$. Powell and Whittaker[2] isolated the lignin from flax shoves by the alkali method. Their lignin preparation appeared to be a fairly homogeneous substance and its composition agreed with the formula $C_{45}H_{48}O_{16}$. In a recent communication[3] the writer reported on a lignin fraction isolated from corn cobs by the alcoholic sodium hydroxide method. All the results obtained agreed closely with the formula $C_{40}H_{46}O_{16}$. The presence of four hydroxyl groups capable of being acetylated and three methoxyl groups was shown.

The two lignin fractions described in this paper were isolated from oat hulls by extracting them successively and exhaustively, first with alcoholic sodium hydroxide solution at room temperature, and then by refluxing with 4% aqueous sodium hydroxide solution. The lignin fraction isolated by the alcoholic sodium hydroxide method was found to have the same composition as that isolated from corn cobs by the same method, namely, $C_{40}H_{46}O_{16}$. In the lignin fraction isolated from corn cobs, however, four hydroxyl groups and three methoxyl groups were shown to be present, whereas the results on the lignin fraction isolated from oat hulls indicate the presence of three hydroxyl and four methoxyl groups. It would appear then, that in the lignin fraction from oat hulls one more hydroxyl group is methylated, the total number of hydroxyl and methoxyl groups being the same in both cases.

The analytical results on the residual lignin fraction isolated by means of aqueous sodium hydroxide solution are more in agreement with that represented by the formula $C_{42}H_{40}O_{15}$. In this lignin fraction three hydroxyl and four methoxyl groups were also shown to be present.

Most investigators have assumed that the alkoxyl groups present in lignin are methoxyls, although few have actually proved this. The fact that a precipitate of silver iodide is obtained when lignin is distilled with hydriodic acid, as in the Zeisel method, in no way implies, of course, that a methoxyl group is present, as other alkoxyl groups would react in a similar manner. In both lignin fractions from oat hulls methoxyl

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[1] Beckmann, Liesche and Lehmann, *Z. angew. Chem.*, 34, 285 (1921).

[2] (a) Powell and Whittaker, *J. Chem. Soc.*, 125, 357 (1924); (b) 127, 132 (1925).

[3] Phillips, THIS JOURNAL, 49, 2037 (1927).

groups only were definitely shown to be present. The alkyl iodide obtained when the lignin was distilled with hydriodic acid was identified as methyl iodide by the method of Feist.[4] Furthermore, by determining the percentage methoxyl of the lignin preparations by the Zeisel[5] method and by the method of Kirpal and Bühn,[6] identical results were obtained. This would necessarily exclude the presence of other alkoxyl groups such as, for example, ethoxyl groups, as the Kirpal and Bühn method is known to give low results when alkoxyl groups other than methoxyl are present.

Experimental

Five hundred grams (464.3 g. of moisture-free material) of oat hulls was treated with 2.5 liters of 2% alcoholic sodium hydroxide solution (prepared by dissolving 50 g. of sodium hydroxide in 1 liter of water and adding sufficient 95% ethanol to make a volume of 2500 cc.) and allowed to stand at room temperature for twenty-four hours. The liquid was then poured off, neutralized with hydrochloric acid and the alcohol was distilled off under reduced pressure. To the aqueous residue, 10 cc. of concentrated hydrochloric acid was added and the precipitated lignin filtered off. The process of extraction with alcoholic sodium hydroxide was repeated until no more lignin was extracted. Five such extractions were required and 2 liters of alcoholic sodium hydroxide solution was used for each extraction. The lignin fractions thus obtained were combined and washed with distilled water until the wash water no longer gave a test for the chloride ion. The crude lignin thus obtained, after being dried in a desiccator over sulfuric acid, amounted to 34.5 g. (6.9% yield calculated on the weight of hulls taken). This was treated with 500 cc. of acetone–alcohol solution (2 volumes of acetone to 1 volume of 95% ethanol), filtered and the alcohol and acetone were removed by distillation under reduced pressure. The lignin thus obtained was washed with water and dried at 56° over sulfuric acid in the vacuum Abderhalden drier. The yield of this purified lignin amounted to 26 g. (5.6% of the weight of the dry hulls taken). That portion of the oat hulls remaining after the treatment with the alcoholic sodium hydroxide solution was washed with water and dried at 100°. The weight amounted to 356 g. (71.2% of the weight of the hulls). A carbon and hydrogen determination made upon the lignin gave the following results.

Anal. Subs., 0.1034, 0.0974; CO_2, 0.2333, 0.2203; H_2O, 0.0542, 0.0507. Found: C, 61.53, 61.68; H, 5.87, 5.83.

The lignin when boiled with 12% hydrochloric acid gave no coloration with aniline acetate paper. The lignin preparation was, therefore, free from furfural yielding compounds.

A methoxyl determination made according to the Kirpal and Bühn[6] modification of the Zeisel[5] method gave the following results.

Anal. Methoxyl.[7] Subs. 0.2038, 0.2022; AgI, 0.2413, 0.2387. Found: OCH_3, 15.64, 15.59; $C:OCH_3 = 10.2 : 1$.

This ratio of percentage of total carbon to the percentage of carbon present in the form of methoxyl indicates the number of carbon atoms present in the substance for each methoxyl group.

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[4] Feist, *Ber.*, **33,** 2094 (1900).

[5] Houben, "Die Methoden der Organischen Chemie," Georg Thieme, Leipzig, 1923, Vol. III, p. 144.

[6] Kirpal and Bühn, *Ber.*, 47, 1084 (1914); *Monatsh.*, 36, 853 (1915).

[7] The methoxyl determinations were made by Mr. Herman Weihe of this Bureau.

In order to prove definitely the nature of the alkoxyl group in this lignin fraction a sample of the material was distilled with hydriodic acid, as in the Zeisel method, and the alkyl iodide absorbed in dimethylaniline, as recommended by Willstätter and Utzinger.[8] The crystalline compound obtained after purification with chloroform melted at 231.6' (wrrected). The melting point of trimethylphenylammonium iodide is recorded by Feist as 211–212°. The above-named compound was accordingly prepared from pure methyl iodide and dimethylaniline and purified by recrystallization from hot water and from 95% ethanol. When analyzed for nitrogen (Kjeldahl) and iodine, the following results were obtained.

Anal. Subs., 1.0000, 1.0000: required 18.6 and 18.4 cc. of 0.2 *N* acid. Subs., 0.3180, 0.3135; AgI, 0.2826, 0.2779. Calcd. for $C_9H_{14}NI$: N, 5.32; I, 48.24. Found: N, 5.21, 5.16; I, 48.03, 47.91.

This compound melted at 231.6° (corrected). The melting point given by Feist is, therefore, incorrect.

The crystalline product obtained from the lignin, as above described, was mixed with some trimethylphenylammonium iodide and the melting point of the mixture taken. It was also found to melt at 231.6° (corrected).

While the above results proved fairly conclusively that the methoxyl group was present in this lignin fraction, it nevertheless could not be accepted as evidence of the absence of other alkoxy groups, although no other crystalline body could be separated from the dimethylaniline mother liquors. Willstatter and Utzinger[8] have described a method for the quantitative separation and estimation of the methoxyl and ethoxyl groups when both are present in the same compound. Essentially, the method consists in absorbing the alkyl iodide in a 10% solution of trimethylamine in absolute alcohol; the tetramethylammonium iodide that is formed is insoluble in absolute alcohol, whereas the trimethylethylammonium iodide is soluble. This method was found, however, to be unreliable, principally because of the fact that the tetramethylammonium iodide is not altogether insoluble in absolute alcohol. For example, when this method was applied to vanillin it was found to yield 16.3% of methoxyl and 4.6% of ethoxyl. The absence of other alkoxyl groups in this lignin fraction was finally proved in an entirely different manner. The method of Kirpal and Biihn is known to give low results when alkoxyl groups other than methoxyl are present,[9] a fact which the writer verified experimentally. The Zeisel method is, however, of more general application, and quantitative results are obtained also when applied to the determination of alkoxyl groups other than methoxyl. It was accordingly only necessary to determine the percentage of alkoxyl (calculated as methoxyl) by both methods in order to prove definitely the presence or absence of alkoxyl groups other than methoxyl in this lignin fraction. The results of the determination of the percentage of alkoxyl (calculated as methoxyl) were as follows.

Anal. Methoxyl (Zeisel method). Subs., 0.3358, 0.3000; AgI, 0.3931, 0.3503. Found: OCH_3, 15.46, 15.42. Methoxyl (Kirpal and Biihn method). Subs., 0.2338, 0.2022; Agl, 0.2413, 0.2387. Found: OCH_3, 15.64, 15.59.

It will be observed that practically the same results were obtained by the two methods. The presence of methoxyl groups only in this lignin fraction must, therefore, be assumed.

From the foregoing data the formula $C_{40}H_{46}O_{16}$ is deduced for this lignin fraction, 782.6: C, 61.35%; H, 5.92%; OCH_3, 15.92%. Four OCH_3 groups are present = $C_{36}H_{34}O_{12}(OCH_3)_4$. The empirical formula of this lignin fraction is the same as that previously8reported for the lignin from corn cobs.

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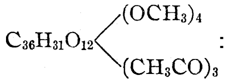
[8] Willstatter and Utzinger, *Ann.*, 382, 148 (1911).

[9] Ref. 5, p. 149.

Preparation of Acetyl Derivative.—To 5 g. of lignin, 10 cc. of acetic anhydride and 3 to 4 drops of concentrated sulfuric acid were added. The reaction mixture was heated on the water-bath under a reflux condenser for one hour. The reaction product was allowed to cool, poured into ice water, filtered, and washed with cold water. The product was allowed to remain in a sulfuric acid desiccator overnight and then dried for twenty-four hours at 56° in a vacuum Abderhalden drier containing sulfuric acid and solid potassium hydroxide. The percentage acetyl was determined by the Perkin[10] method.

Anal. Acetyl. Subs., 0.7011, 0.7793: required 5.50, 6.1 cc. of 0.5 N KOH.



Calcd. for $C_{36}H_{31}O_{12}\begin{cases}(OCH_3)_4\\(CH_3CO)_3\end{cases}$: CH_3CO, 16.4. Found: CH_3CO, 16.8, 16.8.

The dissected formula for this lignin fraction is, therefore, $C_{36}H_{31}O_9(OCH_3)_4(OH)_3$.

Isolation of the Residual Lignin.—Three hundred grams of the residual oat hulls which had been extracted with the alcoholic sodium hydroxide solution in the previous experiment and dried at 105° was treated with one liter of 4% sodium hydroxide and heated at 100° for four hours. This reaction mixture was filtered, and the lignin precipitated by the addition of concentrated hydrochloric acid to the filtrate. The residual oat hulls were again treated with 4% sodium hydroxide solution, and the operation was repeated until the alkaline extract when acidulated with hydrochloric acid no longer gave a precipitate of lignin. The cellulose residue obtained was washed with water and dried at 105°. The yield amounted to 151 g. (50.3% of the weight of the hulls taken). It still contained 3.4% of lignin as determined by the fuming hydrochloric acid method of Willstätter. The crude lignin obtained in the several extraction operations was combined, and when dried at 105° its weight amounted to 18 g. When boiled with 12% hydrochloric acid, this lignin gave a positive test for furfural with aniline acetate paper. It was purified by dissolving it in 500 cc. of 2% aqueous sodium hydroxide and adding to it one liter of 95% ethanol. The precipitate was filtered off, the filtrate was acidified with hydrochloric acid and the alcohol was removed by distillation. The lignin obtained was washed with water until the wash water gave no test for chloride with silver nitrate solution and dried at 105°; yield, 13 g. or 4.3% (calculated on the 300 g. of hulls used). It was an amorphous brown material. The color was darker than that of the lignin obtained by the alcoholic sodium hydroxide method. When distilled with 12% hydrochloric acid the lignin did not give a coloration with aniline acetate paper nor a precipitate with phloroglucinol.

Anal. Subs., 0.0900, 0.0899: CO_2, 0.2123, 0.2123; H_2O, 0.0413, 0.0423. Found: C, 64.33, 64.40, H, 5.13, 5.26.

The alkoxyl groups present in this lignin fraction were shown to be methoxyls. The method previously described for the identification of the alkoxyl groups was used.

Anal. Methoxyl (Kirpal and Buhn method). Subs., 0.3243, 0.4035: AgI, 0.3865, 0.4849. Found: OCH_3, 15.74, 15 88. Methoxyl (Zeisel method). Subs., 0.2018, 0.2130: AgI, 0.2398, 0.2521. Found: OCH_3, 15.70, 15 64. $C:OCH_3 = 21:2$.

Based on the above analytical data, the formula $C_{42}H_{40}O_{15}$ or $C_{38}H_{28}O_{11}(OCH_3)_4$ is assigned for this lignin fraction. The percentage composition for a compound of this formula is: C, 64.27; H, 5.13; OCH_3, 15.80.

Acetyl Derivative.—This was prepared by the method already described. The same method was used for the determination of the percentage acetyl.

Anal. Acetyl. Subs., 1.0575, 1.0421: required 7.99, 7.80 cc. of 0.5 *N* KOH. Calcd. for $C_{38}H_{25}O_{11}(OCH_3)_4(COCH_3)_3$: CH_3CO, 16.4. Pound: CH_3CO, 16.2, 16.1.

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[10] Perkin, Proc. *Chem. Soc.,* 20, 171 (1904).

The dissected formula for the lignin obtained in this fraction is, therefore, $C_{38}H_{25}O_8(OCH_3)_4(OH)_3$.

Summary

1. Two lignin fractions were isolated from oat hulls by extracting them successively and exhaustively, first with 2% alcoholic sodium hydroxide solution at room temperature, and then by refluxing with 4% aqueous sodium hydroxide solution. All the results agree with the dissected formula $C_{36}H_{31}O_9(OCH_3)_4(OH)_3$ for the first lignin fraction and $C_{38}H_{25}O_8(OCH_3)_4(OH)_3$ for the second lignin fraction,

2. The alkoxyl groups present in both lignin fractions were definitely proved to be methoxyls. A method for proving this is described.

3. The melting point of trimethylphenylammonium iodide was found to be 231.6° (corrected) and not 211–212° as recorded in the literature.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

THE EFFECT OF ETHYLENE UPON THE ACTIVITY OF DIASTASE AND INVERTASE

BY D. T. ENGLIS AND C. D. ZANNIS

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With the increasing use of ethylene for the artificial ripening of fruits and vegetables much interest is manifested in the nature and mechanism of the action. In a recent bulletin emphasizing the practical application of the use of the gas, Harvey[1] has appended a very complete bibliography of the literature of the subject. A difference of opinion seems to prevail as to whether the change in the fruits and vegetables induced by the ethylene is chiefly a color change or a genuine ripening in which not only color but the normal accompanying changes in composition take place. Chace and Church,[2] after carrying out a large number of experiments and analyses, conclude that there is no difference in the composition of the edible portion of citrus fruits subjected to the ethylene method of coloring when compared to untreated fruits under the same temperature conditions. Data on other fruits were too meager to permit definite conclusions and did not suggest any changes which would not be caused by heat alone. Harvey[3] insists that ethylene brings about a genuine ripening effect when applied at concentrations of 1 to 1000 of air at 65°F. He believes that the results obtained by Chace and Church were due to the lower concentration of ethylene used, 1 part in 5000 of air. Rosa[4] states that ethylene favors the rate of softening, color change and inver-

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[1] Harvey, Bulletin 247, University of Minnesota Agr. Exp. Sta., October, 1928.

[2] Chace and Church, *Ind. Eng. Chem.*, *19*, **1135** (1927).

[3] Harvey, *Science*, 67,421 (1928).

[4] Rosa, *Hilgardia*, **3,** 421 **(1928).**

sion of sucrose in the later stages of development of certain melons and attributes the effect to the acceleration of enzymic activity. This opinion seems to be more or less general and is concurred in by Regeimbal, Vacha and Harvey,[5] who report that treated bananas have one-fifth to one-fourth more sugar and less starch than the untreated samples. They believe that ethylene increases the activity of diastase and thus favors the conversion of starch to sugar. The respiratory activity was found to treble in a few minutes after treatment and then dropped to a subnormal value. This was ascribed either to an increase in respiratory oxidation or an increase in the permeability of the membranes.

Apparently very little has been done to determine the effect of ethylene upon the activity of enzymes using pure substrate material. One experiment by Regeimbal and Harvey[6] has been carried out with the proteoclastic enzymes of the pineapple and a substrate of pure casein. When the amino nitrogen produced was measured by the Van Slyke method a slightly higher rate of hydrolysis was indicated for the treated material.

Our attention to the effect of ethylene upon the activity of diastase was prompted by the observations of Dickter[7] that sometimes toluene and other antiseptics, which were being investigated in this Laboratory for use in diastase studies, appeared to have a catalytic action upon the hydrolysis of the starch. In 1908 Butkewitsch[8] found that when twigs were cut and stored in water containing chloroform or toluene, the starch-dissolving enzymes came rapidly into action and removed the starch, although in water alone the starch was not affected. These facts seemed to indicate the possibility that the effect of ethylene might be of similar nature. Accordingly, it was planned to determine its influence upon two enzymes concerned with the hydrolysis of carbohydrate material. The enzymes chosen were diastase and invertase.

Experimental

Effect of Ethylene upon Diastase. Materials and Method.—Since it is probable that maltase is present universally in plants? it seemed desirable to select as materials for study some which are reported to contain this component of the amylase system in relatively large amounts. Accordingly, Taka-diastase (Parke-Davis), alfalfa meal and corn meal were selected. Soluble starch (according to Lintner) in a concentration of 2% was used as the substrate.

The optimum P_H for malt amylase has been found[10] to be in the region

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[5] Regeimbal, Vacha and Harvey, Plant *Physiology*, 2,357 (1927).

[6] Regeimbal and Harvey, THIS JOURNAL, 49,1117 (1927).

[7] Dickter, Bachelor of Science "Thesis," University of Illinois, 1927.

[8] Butkewitsch, *Biochem. Z.*, 10, 314 (1908).

[9] Davis, *Biochem.* J.,10, 31 (1916).

[10] Sherman, Thomas and Baldwin, THIS JOURNAL, 41,231 (1919).

of 4.4–5, and it is likely that other plant diastases have a similar optimum. In order to obtain a value near this region a concentrated buffer containing one mole each of sodium acetate and acetic acid per liter was prepared. By diluting this solution with water in a ratio of 1 to 100, the P_H of the resulting solution as determined by the hydrogen electrode was 4.66. In all the experiments the buffer was added to the substrate material so that the final dilution was of the order to give this value.

Experiment I

Procedure.—A liter of 2% starch solution was prepared as directed by Sherman and Thomas.[11] After cooling to room temperature 10 cc. of the acetate buffer was added and the solution mixed thoroughly before making to volume. Then two 450-cc. portions were withdrawn. One was saturated with ethylene by passing the gas into it through a Folin aeration tube. Both portions were warmed to 40° in an electric oven.

Twenty-five one-hundredths g. of Taka diastase was dissolved in 100 cc. of the acetate buffer of P_H 4.66. To each treated and untreated starch solution 25 cc. of Taka-diastase solution was added and the solutions were allowed to digest at 40°. At the end of the periods indicated 100-cc. portions were removed and added to flasks containing 3 g. of dry sodium carbonate to stop the enzymatic action. These solutions were analyzed for total reducing sugar by the Munson and Walker method. A blank was also run in which the starch solution was added to the sodium carbonate before the Taka-diastase was introduced. The results are given in Table I. This experiment indicates that there is no significant difference between the ethylene-treated and untreated samples.

TABLE I

EFFECT OF ETHYLENE UPON THE SACCHARIFICATION OF SOLUBLE STARCH BY TAKA-DIASTASE

EXPERIMENT I

Taka-diastase, 0.0139 g. per 100 cc. of substrate. Substrate, 2% soluble starch. Temperature, 40°

25-Cc. portions		Cu_2O, mg.	Apparent maltose, mg.
Blank		20.3	14.5
Portion A untreated	One-half hour	90.0	75.0
	One hour	152.5	125.1
Portion B, treated with ethylene	One-half hour	88.5	71.6
	One hour	152.9	125.4

EXPERIMENT II

Taka-diastase, 0.00695 g. per 100 cc. of substrate. Substrate, 2% soluble starch. Temperature, 40°

25-Cc. portions		Cu_2O, mg.		Apparent maltose, mg.	
Blank		23.8	24.0	17.7	17.9
Untreated	One hour	59.3	58.3	47.4	46.5
	Two hours	83.2	83.1	67.3	66.4
Treated	One hour	54.5	56.0	43.4	44.6
	Two hours	80.5	84.5	65.0	68.4

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[11] Sherman and Thomas, THIS JOURNAL, 37, 623 (1915).

Experiment II

Ford and Guthrie[12] have found that by using a papain digestion with ground barley malt, a much higher activity was obtained than without it. This was believed to be due to the bringing of endocellular enzymes into solution and preserving them as well. The preserving effect of protein derivatives has been observed and studied by Sherman and Walker.[13]

With the idea that some phase of starch hydrolytic action might have been lessened in the first experiment, **0.2 g.** of asparagin was added as an aid in stabilizing the enzyme solution in the second experiment. The quantity of the enzyme was reduced and the incubation period increased. The results are also given in Table I, and confirm the results of the first experiment.

Experiment III

In order to test another source of diastase, alfalfa meal was added to the starch in place of Taka-diastase and the reaction allowed to proceed at room temperature. The solutions were filtered after inhibition of the enzyme action. The results given in Table II also show no apparent differences in treated and untreated samples.

Table II

Effect of Ethylene upon the Saccharifying Action of the Diastase of Alfalfa Meal

Experiment III

Enzyme source, alfalfa meal, **0.5 g.** per **100** cc. of substrate. Substrate, 2% soluble starch. Temperature, 25°

25-Cc. portion		Cu$_2$O, mg.		Apparent maltose, mg.	
Blank		36.2	36.4	28.1	28.2
Untreated	One hour	68.0	70.0	54.6	56.3
	Two hours	88.1	85.0	71.4	68.8
Treated	One hour	67.2	65.8	53.9	52.8
	Two hours	86.1	82.5	69.7	66.7

In Expt. 4 corn meal was used as a source of the diastase and no additional starch was added. The general procedure devised by Rumsey[14] was followed.

The meal was added to distilled water in the untreated series and in the treated series to water previously saturated with ethylene. The results are given in Table III.

Table III

Effect of Ethylene upon the Saccharifying Action of the Diastase of Corn Meal

Enzyme source, corn meal, **10 g.** per **100** cc. of water. Substrate, starch of corn meal. Temperature, 26°

		Cu$_2$O, mg.				Apparent maltose, mg. per 25 *cc.*			
Untreated	Blank		16.5	16.8			11.7	12.0	
	Sample, one hour	68.2	68.4	67.5	65.2	54.8	55.0	54.2	52.3
Treated	Blank		17.0	16.5			12.1	11.7	
	Sample, one hour	61.7	65.0	64.5	65.0	49.4	52.1	51.7	521

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[12] Ford and Guthrie, Abs. J. *Soc. Chem. Ind.*, 27, 239 (1908).

[13] Sherman and Walker, This Journal, 43, 2469 (1921).

[14] In Morrow, "Biochemical Laboratory Methods," John Wiley and Sons, Inc., New York, 1927, p. 286.

If the ethylene had the property of altering the permeability of the cell walls, freeing the endocellular enzymes and giving an increase in saccharifying power, it should have been apparent in Expts. 3 and 4.

It is unfortunate that the experiments cannot be carried over a **longer** digestion period, but if antiseptics be added to prevent bacterial action, there is the uncertainty as to the effect of the antiseptic itself.

Ethylene and Invertase. Materials and Method.—Invertase was prepared from Fleischmann's yeast according to the method given by Morrow.[15] It was dialyzed in collodion bags as directed.

The sucrose solution was made from pure Domino cane sugar, was of 10% concentration and was buffered with the acetate buffer to a P_H of 4.66. It was divided into two equal portions, one of which was saturated with ethylene. The enzyme was added to each and the progress of hydrolysis followed by the polarimeter. The procedure was also that of Morrow,[16] with the exception that the action was inhibited and equilibrium conditions of the mutarotating mixture were attained by introducing the aliquot withdrawn into a dry flask containing enough solid sodium carbonate to give a concentration of about 1%. Five experiments were run. In the second a slight increase in rate of hydrolysis seemed to occur with the ethylene treated sample. However, it was slight and was never obtained again so it was doubtless due to some error or contamination. Only the results of the third run (See Table IV) will be given, as it is typical of the series.

TABLE IV

EFFECT OF ETHYLENE UPON THE RATE OF INVERSION OF SUCROSE

Enzyme, invertase, 1 cc. per 100 cc. of sucrose. Substrate, 10% sucrose. Temperature, 25.5"

Interval, minutes		0	15	45	75	105	135	165	One day
Polarization in 4-dm. tube, Ventzke °	Treated	74.9	65.9	48.9	33.8	20.9	9.9	1.8	−21.9
	Untreated	74.9	66.0	486	340	21.0	10.1	1.8	−21.9

It seems safe to conclude that ethylene has little or no effect upon the diastases or invertase under the conditions of these experiments. While it does not necessarily follow that the same would be true in a fruit or vegetable with more or less interdependent reactions going on, the results are in harmony with the analyses of Chace and Church and tend to support their conclusion that the ethylene process is primarily concerned with coloration.

Summary

A study has been made of the effect of ethylene upon the activity of diastase and invertase with pure substrate materials.

No acceleration of the saccharifying action of Taka-diastase or alfalfa meal upon soluble starch was observed when the solutions were treated with ethylene. This was also true of the diastase of corn meal acting upon the starch of the grain.

A determination of the rate of hydrolysis of sucrose using the polarimetric method indicated no benefit due to ethylene.

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[15] Ref. 14, p. 281.

[16] Ref. 14, p. 283.

These observations are in accord with the idea that the effect of ethylene in the ripening of fruits and vegetables is primarily concerned with color change rather than a true ripening process.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 235]

A NEW TEST FOR DISTINGUISHING THE PRIMARY, SECONDARY AND TERTIARY SATURATED ALCOHOLS

BY HOWARD J. LUCAS

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The most convenient method of distinguishing the three classes of alcohols is that given by Kamm,[1] who makes use of the difference in the rate with which the alcohols react with hydrobromic acid.

The readiness with which tertiary butyl alcohol reacts with cold concentrated hydrochloric acid[2] suggests this reaction as a means of distinguishing the tertiary alcohols.

Secondary but not primary alcohols react at room temperature with concentrated hydrochloric acid containing zinc chloride in the mole ratio of one to two. This reagent, which was first employed by Norris and Taylor[3] at higher temperatures for the preparation of alkyl chlorides, has recently been used for preparing 2-chloro- and 3-chloro-3-ethylpentane from the corresponding alcohols at room temperature.[4]

Reagent.—The hydrochloric acid–zinc chloride reagent is made by dissolving 136 g. (1 mole) of anhydrous zinc chloride in 105 g. (1 mole) of concentrated hydrochloric acid with cooling. Either Baker's zinc chloride, fused sticks, or a technical powder may be used.

Procedure.—To 2 ml. of the alcohol in a vial or test-tube is quickly added 12 ml. of the hydrochloric acid–zinc chloride reagent at 26–27°. The mixture is shaken and the tube is closed with a cork. Alcohols lower than hexyl are soluble, but tertiary alcohols react so fast and the separation of the tertiary chloride proceeds so rapidly that two phases are observed from the time of mixing. On standing, within five minutes or less the clear solution becomes cloudy in the case of the secondary alcohols and undergoes no change other than darkening in the case of the primary. After one hour a distinct upper layer is visible in the case of all of the secondary alcohols except *iso*propyl. The results are shown in the table.

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[1] Kamm, "Qualitative Organic Analysis," John Wiley and Sons, Inc., New York, **1923;** Kamm and Marvel, THIS JOURNAL, **42,** 299 (1920).

[2] Davis and Murray, Ind. *Eng. Chem.*, 18,844 (1926); "Organic Syntheses," John Wiley and Sons, Inc., New York, **1928,** Vol. VIII, p. 50.

[3] Norris and Taylor, THIS JOURNAL, **46,** 753 (1924).

[4] Lucas, *ibid.*, 51, 248 (1929).

TABLE I

BEHAVIOR OF ALCOHOLS WITH HYDROCHLORIC ACID–ZINC CHLORIDE REAGENT AT 26°

Clear solutions	Clear solutions becoming cloudy within five minutes
CH_3OH C_2H_5OH CH_2OHCH_2OH[a]	$CH_3CHOHCH_3$[a] $CH_3CHOHCH_2CH_3$[c]
CH_2ClCH_2OH[a] $CH_3CH_2CH_2OH$[a]	$CH_3CHOHCH_2CH_2CH_3$[a,c]
$CH_3(CH_2)_2CH_2OH$[a] $(CH_3)_2CHCH_2OH$[a]	$CH_3CHOHCH(C_2H_5)_2$[d]
$(CH_3)_2CHCH_2CH_2OH$[b]	$CH_3CH_2CHOHCH_2CH_3$[a]

[a] Eastman's. [b] Merck's. [c] Stanco Distributors, New York, through the courtesy of Mr. C. L. Bowman. [d] Lucas, ref. 4.

To distinguish with certainty between tertiary and secondary alcohols, another sample of the alcohol is mixed with concd. hydrochloric acid alone. Tertiary butyl and amyl alcohols immediately react to form the insoluble chloride, which rises to the surface in a few minutes. The solutions obtained from the secondary alcohols should remain clear.

Discussion.—With the exception of the unsaturated primary alcohol, allyl, which reacted within seven minutes, none of the primary alcohols tried gave the test with the zinc chloride–acid mixture, while all of the secondary did. Even though the alcohol does not mix with the reagent, it is still possible to distinguish between those which react and those which do not, since in the former case the aqueous phase takes on a milky appearance due to the separation of the finely divided chloride. Thus both 1-hexanol and 2-hexanol gave two phases, but only in the case of the latter did the lower phase take on the cloudy appearance characteristic of the reaction. The secondary alcohol, 3-ethyl-2-pentanol, behaved like the tertiary alcohols in that the chloride separated within one or two seconds after mixing.

In carrying out these tests with the alcohols the production of the second phase cannot be taken as the sole criterion of the reaction; the formation on standing of a distinct upper layer must be an accompanying phenomenon[5] For example, a 20% solution of 2-butanol in 1-butanol gave *a* slight cloudiness within six minutes at 26°; this increased somewhat on standing. However, even after ten hours there was no distinct upper layer but only a few small drops of a second phase made visible by gentle agitation. A 10% solution of 2-butanol in 1-butanol gave a slight cloudiness in thirty minutes, increasing on standing. With concentrated hydrochloric acid alone a 10% solution of tertiary butanol in 2-butanol give an immediate cloudiness, one of 5% reacted in thirty seconds, while one of 4% failed to give the test. In none of these cases was an upper layer apparent. It is thus evident that when the reaction proceeds so as to produce a cloudiness without the upper layer developing, an alcohol is present as an impurity.

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[5] The upper layer did not form with *iso*propyl alcohol, presumably because of the volatility of the chloride.

Apparently, some of the alcohols used in this work were not of the highest purity, since the 2-propanol, 2-pentanol and 3-pentanol gave weakly cloudy solutions with concd. hydrochloric acid alone. However, the tests for distinguishing the alcohols as developed herein are believed to be reliable, since the amounts of these impurities were small.

The reaction time is lower if the proportion of reagent to alcohol is smaller, or if the temperature is lower. At a six to one ratio 2-butanol gave the test in two minutes at 26° and in seven minutes at 20°; at a four to one ratio, in five and nine minutes, respectively; while at a two to one ratio (approximately mole per mole) the test was given in two and one-half to three hours.

Summary

The lower saturated alcohols may be readily differentiated by the fact that the tertiary alcohols react rapidly with concentrated hydrochloric acid alone to form insoluble liquid chlorides, the secondary react with hydrochloric acid–zinc chloride mixture within five minutes at 26°, while the primary alcohols react with neither. Allyl alcohol resembles a secondary alcohol.

The presence of a secondary or a tertiary alcohol in another compound may he demonstrated by these reagents, provided the concentration of the alcohol is not too low.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

SYNTHESIS OF N-PHENYLPYRROLIDINE AND N-HEXAHYDROPHENYLPYRROLIDINE

BY LYMAN C. CRAIG WITH R. M. HIXON

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In a study of the insecticidal action of nicotine and related compounds, pyrrolidine and a series of its derivatives were desired. The methods reported in the literature[1] for the preparation of pyrrolidine are all difficult and tedious. During the progress of the studies reported below, Anderson and McElvain[2] published their work on the catalytic reduction of pyrrole using specially purified pyrrole, glacial acetic acid, a large quantity of platinum-oxide platinum black catalyst and shaking for four to five days.

The catalytic reduction is much more convenient with the platinum-oxide platinum black catalyst using as a solvent absolute alcohol contain-

[1] Ciamician and Magnaghi, *Ber.*, 18, 2079 (1885); Ladenburg, *ibid.*, 19, 780 (1886); 20,2215 (1887); Wohl, Schafer and Theile, *ibid.*, 38,4157 (1906); Gabriel, *ibid.*, 42, 1254 (1912); Keil, *ibid.*, 59,2816 (1926); Putochin, *ibid.*, 55, 2742 (1922); Willstätter and Hatt, *ibid.*, 45, 1477 (1912); Willstatter and Waldschmidt, *ibid.*, 54, 125 (1921); Hess, *ibid.*, 46,3113 (1913).

[2] Anderson and McElvain, THIS JOURNAL, 51, 887 (1929).

ing a slight excess over an equivalent of hydrogen chloride. With the latter solvent 0.2 g. of catalyst can be used for three successive reductions of 10-cc. portions of pyrrole, the reduction being complete in six hours and the yield being 80% of the theoretical.

A mixture of α- and β-methylpyrroles was prepared according to the method reported by Anderson and McElvain. Reduction of these compounds by the above method was as unsuccessful as in glacial acetic acid. A small amount of reduction did take place but the basic oil obtained in recovery proved to be pyrrolidine, which indicated the presence of pyrrole in the fraction taken. These compounds are more unstable and go over to pyrrole red derivatives much more easily than does pyrrole.

In the N-substituted pyrrolidine series, the aliphatic derivatives can be prepared by treating the free base with RX. The aromatic derivatives are more difficult to prepare. It was expected that N-phenylpyrrole could be selectively reduced in alcohol and hydrochloric acid. This is not the case for under these conditions the benzene ring apparently reduces as easily as the pyrrole ring. Five moles of hydrogen are rapidly absorbed (two and one-half hours) and a constant boiling tertiary base is obtained which is N-hexahydrophenylpyrrolidine. If the reduction is stopped when two moles of hydrogen have been absorbed, some unreduced N-phenylpyrrole and a base which does not have a constant boiling point (206–247°) are the products obtained. The identity of the N-hexahydrophenylpyrrolidine was proved by condensing bromocyclohexane with pyrrolidine.

In attempting to prepare the N-phenylpyrrolidine, several other methods were tried without success. LeSueur[3] has prepared the compound N-phenyl-α,α'-dicarboxypyrrolidine. This compound evolves carbon dioxide when subjected to dry distillation under reduced pressure. Small amounts of N-phenylpyrrolidine are produced but the method cannot be recommended for purposes of preparation.

Piperidine when heated in a sealed tube with bromobenzene to 250–260° gives a small yield of N-phenylpiperidine.[4] The analogous synthesis fails with pyrrolidine although reaction takes place at 220°. Apparently ring cleavage takes place under these conditions since a very stable amine was isolated with too high a ratio between hydrogen and carbon to permit of its containing a benzene nucelus.

The N-phenylpyrrolidine can be prepared with satisfactory yields by condensing aniline with tetramethylene chloride.

Experimental

Preparation of Pyrrole.—The method of preparation used was that of Schwanert.6 Five hundred grams of mucic acid was converted to the neutral ammonium salt with

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[3] LeSueur, *J. Chern. Soc.*, 95, 273 (1909).

[4] Lellmann and Geller, Ber., 21, 2279 (1888).

[5] Schwanert, *Ann.*, 116,278 (1860).

excess ammonia and subjected to dry distillation in an iron retort. The pyrrole was extracted from the distillate with ether, the ether evaporated off and the residue distilled. Fifty cc. of a fraction boiling at 125 to 130° was obtained which is 32% of the theoretical yield. By use of glycerol according to the method of Goldschmidt,[2,6] a higher yield is obtained (40–50% of the theoretical) but dry distillation is much less trouble and considering the relative price of mucic acid and glycerol is to be preferred.

Reduction of Pyrrole to **Pyrrolidine.**—The platinum-oxide platinum black catalyst was prepared according to the method of Adams and Shriner.[7] The shaking machine was a modification of that ordinarily used in that the connections and tubing were all metal with a rubber gasket for the bottle. A pressure of approximately 90 lb. was used. Pyrrole not freshly distilled and colored reduced slowly if at all. Commercial samples freshly distilled reduced as easily as the samples freshly prepared from ammonium mucate. The pyrrole was dried over anhydrous calcium chloride before the final distillation.

To 100 cc. of absolute alcohol, 0.2 g. of catalyst, 10 cc. of pyrrole and a slight excess over an equivalent of concentrated hydrochloric acid (6 cc.) were added. The pyrrole reduced the catalyst at once; previous reduction of the catalyst before addition of pyrrole did not increase the rate of reduction. Absolute alcohol containing a calculated amount of dry hydrogen chloride did not increase the rate of reduction, although there is less pyrrole red formed. If 95% alcohol is used the reduction is slower and there is considerable pyrrole red formed. The reduction was completed in about six hours. The catalyst was allowed to settle and the reduction products decanted. To the catalyst fresh portions of alcohol, acid and pyrrole were added. A third reduction could also be run on the same catalyst without seriously impairing the efficiency. No occasion was had to run more than three reductions on the same catalyst but there appeared to be no tendency for it to become poisoned if good pyrrole was used. After decantation, the alcohol was removed by evaporation under reduced pressure, the unreduced pyrrole was extracted with ether, solid potassium hydroxide was added to the solution of the salt until an oil separated and the oil finally dried over solid potassium hydroxide. It distilled at 86–88', small residues of a high-boiling fraction being left behind. Derivatives showed the constant boiling fraction to be pyrrolidine.

Preparation of **N-Phenylpyrrole.**—The method of preparation was essentially that of Feist.[8] Two hundred grams of mucic acid was added with constant stirring to an excess of aniline heated to a temperature just below boiling. This mixture was then placed in an iron retort and heated until no more liquid came over. The distillate was extracted with ether and the aniline removed by washing with a dilute solution of hydrochloric acid. After evaporating off the ether, the residue was distilled under reduced pressure; yield, 25%. As N-phenylpyrrole colors slightly on standing, it was recrystallized from 95% alcohol immediately before use. It crystallized in lustrous leaves, melted at 60–61° and boiled at 234°, as reported in the literature.

Reduction of N-Phenylpyrrole to **N-Hexahydrophenylpyrrolidine.**—A 10-g sample was dissolved in 100 cc. of absolute alcohol, a slight excess over one equivalent of concd. hydrochloric acid and 0.2 g. of catalyst were added. The reduction was rapid, being complete in two and one-half hours, 5 moles of hydrogen being absorbed. The reaction mixture was colorless and on recovery in the same way as with pyrrolidine, a constant boiling oil (209–211°) was obtained, the yield being quantitative. It did not react with phenyl isothiocyanate. It gave a picrate which on repeated crystallization from alcohol

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[6] Goldschmidt, *Z. Chem.*, 280 (1867); Khotinsky, *Ber.*, 42, 2506 (1909).

[7] Adams and Shriner, THIS JOURNAL, 45,2171 (1923).

[8] Feist, Ber., 35, 1655 (1902).

melted at 163–164°. The hydrochloride was hygroscopic and not suitable for a melting point determination.

Stopping the reduction when two moles of hydrogen were absorbed gave 6 cc. of an oil that did not show a constant boiling point (206–247°). It was probably a mixture of N-phenyl- and N-hexahydrophenylpyrrolidine. Separation by chemical means failed and all attempts at fractional crystallization of picrates gave only the N-hexahydro derivative.

Proof of Structure of N-Hexahydrophenylpyrrolidine.—Six cc. of pyrrolidine and an excess of bromocyclohexane were refluxed for two hours. Two layers were present, showing that a reaction had taken place. The base when recovered in the usual way with solid potassium hydroxide gave a small amount of a high-boiling fraction. A picrate of this recrystallized from alcohol melted at 163°. Mixed melting points proved its identity with that from the reduction product of N-phenylpyrrole.

Preparation of N-Phenylpyrrolidine.—To 8 g. of tetramethylene chloride[9] two equivalents of freshly distilled aniline were added and the mixture kept at 100° for four hours. On cooling, the mixture became solid with crystals. A dilute solution of hydrochloric acid was added and the unreacted tetramethylene chloride removed by extracting with ether. The free base was liberated by strong caustic and the two layers separated. The excess aniline was removed from the oily layer with benzenesulfonyl chloride in dilute alkali. The tertiary amine fraction was extracted with ether and precipitated with dry hydrogen chloride. The free base was then recovered and dried with potassium hydroxide. It had a slight red color and did not react with acetyl chloride. When the free base was subjected to distillation at atmospheric pressure, the boiling point did not remain constant and a colorless oil distilled over that reacted vigorously with acetyl chloride. Evidently the pyrrolidine ring must partially rupture during distillation. The undistilled base formed a chloroplatinate that crystallized from alcohol acidified with hydrochloric acid in yellow needles and melted with decomposition at 174–175° varying slightly with the rate of heating.

Anal. Calcd. for $(C_{10}H_{13}N)_2 \cdot H_2PtCl_6$: Pt, 27.7. Found: Pt, 27.6, 27.7.

A crystalline picrate could not be obtained for the N-phenylpyrrolidine. On addition of an ether solution of oxalic acid to an ether solution of the base, a white precipitate formed that could be recrystallized from a mixture of acetone and petrolic ether; m. p. 156". The only oxalate that corresponds to the analysis is the tetroxalate with $^1/_2$ molecule of water of crystallization.

Anal. Calcd. for $C_{10}H_{13}N \cdot (COOH)_4 \cdot {}^1/_2H_2O$: C, 49.9; H, 5.36. Found: C, 50.00, 50.10; H, 5.46, 5.52.

Dry Distillation of α,α'-Dicarboxy-N-phenylpyrrolidine.—This compound could be best prepared by the method given by LeSueur. On dry distillation of α,α'-dicarboxy-N-phenylpyrrolidine under reduced pressure, an oil with a slight red color distilled over. It gave an oxalate that corresponded with that of the N-phenylpyrrolidine reported above. Mixed melting points showed the oxalates to be identical.

Reaction of Pyrrolidine with Bromobenzene.—Ten cc. of pyrrolidine was heated with an equivalent of bromobenzene in a sealed tube at 220° for six hours. Experiment had shown this to be the minimum temperature at which reaction takes place. Two layers had separated in the tube and on recovery and distillation 6 cc. of a very stable oil (b. p. 250 to 256°) was obtained. It reacted vigorously with acetyl chloride but a crystalline derivative could not be isolated. It gave a non-hygroscopic hydrochloride when dry hydrogen chloride was passed through its ether solution. This was recrystallized from absolute alcohol and analyzed.

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[9] Prepared from pyrrolidine according to the method of Braun and Beschke, *Ber.*, 39, 4119 (1906).

Anal. Found: C, 52.8, 53.1; H, 10.02, 10.05; Cl, 26.43, 26.46.

The ratio of carbon to hydrogen is too high for this compound to contain a benzene ring. When shaken with water the free base formed leaf-like crystals that melted slightly above room temperature. It also gave a picrate with a melting point of 155°.

Summary

It has been shown that pyrrole can be reduced easily to pyrrolidine in absolute alcohol–hydrochloricacid solution This method is more rapid and convenient than the glacial acetic acid method.

Reduction of N-phenylpyrrole yields N-hexahydrophenylpyrrolidine. The reduction cannot be stopped at the intermediate N-phenylpyrrolidine.

Bromobenzene does not react with pyrrolidine as with piperidine. Pyrrolidine is less stable and rupture of the ring appears to take place.

N-phenylpyrrolidine can be prepared in satisfactory yields by condensing tetramethylene chloride with aniline. The compound can also be prepared by dry distillation under reduced pressures of α,α'-dicarboxy-N-phenylpyrrolidine but the yields are very low.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE COLLEGE OF THE CITY OF NEW YORK]

THE FATTY ACIDS ASSOCIATED WITH WHEAT STARCH

BY LEO LEHRMAN

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The occurrence of fatty acids combined with carbohydrate in several natural starches is quite well known.[1] In two of these starches, corn and rice, the fatty acids have been determined qualitatively and quantitatively.[2] A review of the literature revealed that there is very little known about the non-carbohydrate constituents: if any, of wheat starch. Should fatty acids be found combined with carbohydrate in wheat starch, it is logical to assume that there are at least two components, a- and β-amylose,[3] comparable to those found in corn and rice starch and that the fatty acids constitute part of the a-amylose component.[3]

The work was accordingly carried out first with the object of establishing whether or not fatty acids occurred combined with carbohydrate. After this had been shown, the next thing was to determine the total amount of fatty material, "fat by hydrolysis,"[1b] which would give a means of comparison with other starches. A qualitative and quantitative analysis by means of iodine numbers of the fatty acids[2] present in the "fat by

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[1] (a) Sostegni, *Gazz. chim. ital.*, 15, 376 (1885); (b) Taylor and Nelson, THIS JOURNAL, 42, 1726 (1920); (c) Aoi, *J. Chem. Soc. Japan, 44,* 755 (1923).

[2] (a) Taylor and Lehrman, THIS JOURNAL, 48, 1739 (1926); (b) Lehrman, *ibid.*, 51, 2185 (1929).

[3] Taylor and Iddles, Ind. *Eng. Chem., 18,713 (1926).*

hydrolysis" would be important in that it would give additional information in the study of the starches.

As in previous work,[2] the probable absence of sterols and other substances that might occur in the starch and be present in the liberated fatty acids was shown; also a search for glycerol[2b] in the aqueous filtrate from the hydrolysis was negative, indicating that the fatty acids were not present extraneously in the starch. In the part of the work on the oxidation of the unsaturated fatty acids to hydroxy compounds by means of potassium permanganate in alkaline solution,[4] it was found that all of the more unsaturated (two double bond) fatty acid was changed before any of the less unsaturated (one double bond) fatty acid.

Experimental Part

Mixed Fatty Acids from Wheat Starch.—The wheat starch[4a] was extracted for several hours using petroleum ether and showed a negligible amount of extractable material. A total of twenty pounds, used in five-pound quantities, was required for the work. The starch was hydrolyzed using hydrochloric acid,[2b] five pounds yielding 22.26 g. of a light yellow colored fatty solid corresponding to 0.95% "fat by hydrolysis."

Examination of Filtrate for Glycerol.—The filtrate from the hydrolysis was extracted with chloroform and after the chloroform had evaporated an extremely small amount of brown solid, which smelled of glucose, remained. This brown solid was tested for glycerol[5] with negative results.

Isolation and Identification of Saturated Fatty Acid.—In the course of the separation of the unsaturated fatty acids from the saturated by means of the magnesium soap–alcohol method,[2a] the insoluble magnesium soap was decomposed by heating with concentrated hydrochloric acid. After cooling, a fatty solid layer which was floating on top was removed, dried and dissolved in ether. The solution was dried over anhydrous calcium chloride together with some calcium carbonate in order to remove any hydrochloric acid that might be present. The ether was poured off and allowed to evaporate, leaving a very light yellow colored fatty solid. This was dissolved in alcohol, chilled in an ice-salt bath and the solid quickly filtered by means of suction. This process was repeated until a pure white solid was obtained which was then crystallized from alcohol, when it gave a melting point of 62°.

The phenylhydrazide was made[6] and gave a melting point of 110°.[7]

The molecular weight of the acid was determined by dissolving a weighed amount in methyl alcohol and titrating with a standardized solution of barium hydroxide in methyl alcohol, using phenolphthalein as the indicator?

Anal. Calcd. for palmitic acid, $C_{16}H_{32}O_2$: mol. wt., 256.3. Mol. wt. found: (monobasic acid) 249. Calcd.: C, 74.91; H, 12.59. Found: C, 75.10; H, 12.48.

From the above data the presence of palmitic acid in the mixed fatty acids is shown.

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[4] Lapworth and Mottram, *J. Chem. Soc.*, 127, 1628 (1925).

[4a] The author wishes to thank Stein, Hall and Co., Inc., New York City, for their kindness in supplying this material.

[5] Gettler, *J. Biol. Chem.*, 42, 311 (1920).

[6] Brauns, THIS JOURNAL, 42,1480 (1920).

[7] J. van Alphen, *Rec. trav. chim.*, 44, 1064 (1925).

[8] Escher, *Helv. Chim. Acta*, 12, 103 (1929).

Identification of Unsaturated Fatty Acids

A. Oxidation.—The mixture of unsaturated fatty acids separated from the saturated fatty acid by means of the magnesium soap–alcohol method[2'] was a light brownish colored oil. A 3-g. portion of this mixture was oxidized with potassium permanganate in alkaline solution.[4] The white solid oxidized acids were then extracted with chloroform in order to make a separation[zb] of the oxidized acids, if any. On evaporation of the chloroform a fatty material was obtained which was reoxidized and gave an oxidized product different from the one obtained in the first treatment.

The solid oxidized product (residue from the chloroform extraction) was dissolved by prolonged extraction with ether and the solvent allowed to evaporate. The residue was a white solid melting at 154–156°. This solid was repeatedly extracted with hot water and the solution allowed to cool slowly, whereupon silky white crystals were obtained. These crystals were filtered off, recrystallized from water and dried, giving a melting point of 154–155°. The analytical data indicated the presence of linolic acid in the mixture of unsaturated fatty acids.

Anal. Calcd. for tetrahydroxystearic acid, $C_{18}H_{36}O_6$: C, **62.02**; H, **10.42.** Found: C, **62.17;** H, 10.27.

The product of the second oxidation was dissolved by extraction with anhydrous ether and after the solvent evaporated a white solid remained which gave a melting point of **126.5–127.5".** This was recrystallized from anhydrous ether, giving a melting point of **126–127°.**

The barium salt was made[8] and gave a melting point of **216°,** darkening at 214°.

The molecular weight of the oxidized acid was determined as previously in the case of palmitic acid? The analytical results indicate the presence of oleic acid in the mixture of unsaturated fatty acids.

Anal. Calcd. for dihydroxystearic acid, $C_{18}H_{36}O_4$: mol. wt., **316.3.** Found: **292.5.** Calcd.: C, **68.29;** H, **11.47.** Found: C, **68.31;** H, **11.12.**

The fact that all the tetrahydroxystearic acid and none of the dihydroxystearic acid is found in the product of the first oxidation apparently indicates that all of the linolic acid is oxidized before any of the oleic acid. This is further shown by the absence of tetrahydroxystearic acid in the product of the second oxidation.

The filtrate from the first oxidation was now examined for higher hydroxy acids,[9] but the results were negative, indicating the absence of acids more unsaturated than linolic in the mixture of unsaturated fatty acids.

Another portion, 4 g., of the mixture of unsaturated fatty acids was oxidized in glacial acetic acid by perhydrol **(30%** hydrogen peroxide),[10] but no tangible results could be obtained.

B. **Bromination.**—A 2-g. portion of the mixture of unsaturated fatty acids was brominated,[11] and gave no ether-insoluble bromides, indicating the absence of acids more unsaturated than linolic in the mixture of unsaturated fatty acids, which bears out the results as obtained by oxidation. After evaporation of the ether, the residue was recrystallized from petroleum ether, yielding white crystals, m. p. 113–114°.

Anal. (Carius). Calcd. for tetrabromostearic acid, $C_{18}H_{32}O_2Br_4$: Br, **53.33.** Found: Br, **53.24.**

These results are additional evidence of the presence of linolic acid in the mixture of unsaturated fatty acids.

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[9] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," The Macmillan Company, New York, **1913,** 5th ed., Vol. I, p. **564.**

[10] Hilditch and Lea, **J.** *Chem. Soc.*, **1580 (1928).**

[11] Ref. **9,** p. **573.**

The petroleum ether from the recrystallization of the tetrabromostearic acid was allowed to evaporate, giving a dark brown, thick mass. A portion of this was boiled with concentrated nitric acid to which some solid silver nitrate had been added. On addition of water a heavy precipitate of silver bromide was obtained. This indicates the probable existence of dibromostearic acid, which in turn shows the presence of oleic acid in the mixture of unsaturated fatty acids.

Examination for Other Substances.—The result of a sodium fusion on the mixed fatty acids showed the absence of nitrogen, sulfur and halogens. A fusion of another sample of the mixed fatty acids with a mixture of equal parts of sodium carbonate and sodium nitrate showed the absence of phosphorus.

During the alcoholic saponification of the mixed fatty acids necessary in the preparation of the magnesium soaps,[2a] no unsaponifiable matter was noticed. The Liebermann–Burchard test for phytosterol[12] was negative. The test with 1% alcoholic digitonin[13] was negative. The method of Holde and Gorgas[14] also gave negative results for unsaponifiable matter.

The results given above show the presence of three fatty acids, that is, palmitic, oleic and linolic, and the probable absence of other substances in the fatty acid mixture obtained by extracting the solid material resulting from the hydrolysis of wheat starch.

Determination of Iodine Numbers and Amounts of the Fatty Acids.—Knowing what fatty acids were present, the amount of each one was calculated from the determinations of the iodine numbers[2a] of the mixed and unsaturated fatty acid portions.

TABLE I

RESULTS OF DETERMINATIONS

Fatty acid sample	Weight, g.	Iodine number
Mixed	0.2801	80 36
Mixed	.2098	81.66
Unsaturated	.1324	123.6
Unsaturated	.1350	124 8

TABLE II

RESULTS OF CALCULATIONS

Fatty acid	Percentage
Palmitic	35
Oleic	41
Linolic	24

Summary

The percentage of "fat by hydrolysis" from wheat starch has been determined.

It has been shown that in the oxidation by potassium permanganate in alkaline solution of a mixture of oleic and linolic acids, all the linolic acid is changed before any of the oleic acid is affected.

The fatty acids (saturated and unsaturated) liberated by the hydrolysis of wheat starch free from extraneous material have been identified and their amounts determined.

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[12] Ref. 9, p. 270.

[13] Ref. 9, p. 264.

[14] Holde and Gorgas, Chem. *Umschau Fette, Oele, Wachse Harze*, **32**, 314 (1925); 33, 109 (1926).

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

STUDIES OF CONJUGATED SYSTEMS. III. THE CHLORINATION OF VINYLACRYLIC ACID

BY IRVING E. MUSKAT AND BRUNNER C. BECKER

RECEIVED SEPTEMBER 18, 1929 PUBLISHED FEBRUARY 6, 1930

In continuation of our studies[1] on the addition reactions of conjugated systems we have made an investigation on the chlorination of vinylacrylic acid. A review of previous work on the addition reactions of vinylacrylic acid has been reported in an earlier paper.[1b]

Vinylacrylic acid was prepared according to the method of Muskat, Becker and Lowenstein,[1b] by condensing acrolein with potassium bisulfite and treating the resulting addition product with malonic acid. The chlorination of vinylacrylic acid was then studied. It was found that vinylacrylic acid absorbed two atoms of chlorine to give a dichloride which boiled at 153° under 10-mm. pressure. The chlorination was carried out under varied experimental conditions, but in no case did we obtain a different dichloride. The dichloride is unstable, particularly toward heat and alkali, and readily loses hydrogen chloride.

The structure of the dichloride was determined by ozonizaticn. Three dichlorides are theoretically possible, depending on whether 1,2-, 1,4- or 3,4-addition takes place. On ozonizing the vinylacrylic acid dichloride, it was possible to isolate a 75% yield of oxalic acid, which was identified by its melting point and a melting point of a mixture with a sample of known origin. The second oxidation product, the α,β-dichloro propionic aldehyde was also isolated and identified. A number of ozonizations were made but in no case was it possible to obtain even the slightest indication of the presence of any of the aldehydes or acids to be expected from the oxidation of compounds resulting from the 1,2- or 1,4-addition of chlorine. This proves beyond any doubt that chlorine adds to vinylacrylic acid in the 3,4-position and not in the 1,4-position as is the case with hydrogen.[2]

We were not able to prepare a tetrachloride of vinylacrylic acid, even by allowing to stand with chlorine under pressure for several days. The dichloride can be reduced easily with zinc dust to the original vinylacrylic acid.

On distilling the dichloride under reduced pressure, decomposition occurred with the liberation of hydrogen chloride. A lower-boiling fraction distilled over which partially solidified on standing. This solid was identical with the one obtained by the distillation of vinylacrylic acid dibromide,[1b] which was proved to be a γ-lactone having the structure

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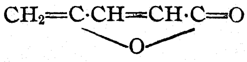
[1] (a) Muskat and Huggins, THIS JOURNAL, 51,2496 (1929); (b) Muskat, Becker and Lowenstein, *ibid.*, 52, 326 (1930).

[2] Thiele, Ber., 35,2320 (1902); see also Doebner, *ibid.*, 35, 1136 (1902).

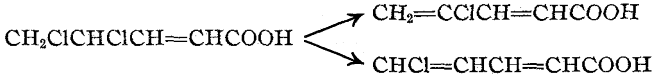


$CH_2{=}C{\cdot}CH{=}CH{\cdot}C{=}O$ (with O bridging C-2 and C-5)

When vinylacrylic acid dichloride was treated with two molar equivalents of sodium hydroxide, the temperature being kept at about zero degrees, the soluble sodium salt of monochlorovinylacrylic acid was formed in almost theoretical yield. The free acid was obtained by acidifying the alkaline solution with cold dilute acids.

Chlorovinylacrylic acid is a light yellow, crystalline compound, very soluble in the ordinary organic solvents and rather unstable. It readily polymerizes to a light yellow solid which is insoluble in all ordinary organic solvents with the exception of acetone. Due to its ease of polymerization it was not possible to obtain a sharp melting point. It melted at about 94°.

It may be seen readily from the structure of the vinylacrylic acid dichloride that hydrogen chloride may be eliminated in either of two ways



$$CH_2ClCHClCH{=}CHCOOH \begin{cases} \rightarrow CH_2{=}CClCH{=}CHCOOH & (A) \\ \rightarrow CHCl{=}CHCH{=}CHCOOH & (B) \end{cases}$$

The structure of the monochloride was proved by further chlorinating it to the chlorovinylacrylic acid dichloride and studying the oxidation products of the trichloride formed.

Chlorovinylacrylic acid readily absorbed a molecule of chlorine to give a trichloro derivative, boiling at 162° under 8-mm. pressure. On standing it solidified to a solid melting at 132°. There are six trichlorides theoretically possible depending on the A or B structure of the monochloride and the type of addition, 1,2-, 1,4- or 3,4-, taking place.[3]

The chlorovinylacrylic acid dichloride was ozonized in the usual manner. It was possible to recover oxalic acid (53% yield), which was identified by its melting point and a melting point of a mixture with a sample of known origin, and also α,α,β-trichloropropionic aldehyde, which was also identified. This proves beyond any doubt that 3-4 addition of chlorine had again taken place, giving rise to a trichloride of structure, CH_2ClCCl_2-$CH{=}CHCOOH$, and therefore the structure of the monochloride must be as represented by (A), $CH_2{=}CClCH{=}CHCOOH$.

The experimental results recorded here lend support to the Hinrichsen view of addition to conjugated systems as contrasted with the Thiele view. That is, the type of addition—1,2-, 1,4- or 3,4—to conjugated systems is a function not only of the conjugated compound itself, but also depends on the nature of the addendum. Thus vinylacrylic acid adds hydrogen in the 1,4-position, while it adds bromine and chlorine in the 3,4-position. It seems very likely in the light of more recent work by Ingold, Prevost, Farmer, Claisen, and others, that even in those cases

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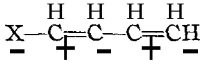
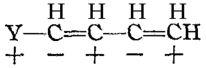
[3] See Muskat, Becker and Lowenstein, THIS JOURNAL, 52, 328 (1930), for the six possible structures.

where the substituents are found in the 1,4-position, it is not necessarily due to 1,4-addition, but rather to a condition of equilibrium in three-carbon systems containing a double bond.

The elimination of the chlorine atom from the vinylacrylic acid dichloride from the 4-position rather than from the 3-position could be readily interpreted if it were assumed that the conjugated system has an electronic arrangement similar to that suggested by Stieglitz[4] for the aromatic nucleus. Thus, we could develop the following electronic structures for conjugated systems.[5]



$$\begin{array}{ccccccccc} & & H & & H & & H & & H\\ X & - & C & = & C & - & C & = & CH\\ - & & + & & - & & + & & - \end{array}$$

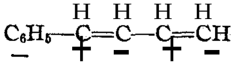


$$\begin{array}{ccccccccc} & & H & & H & & H & & H\\ Y & - & C & = & C & - & C & = & CH\\ + & & - & & + & & - & & + \end{array}$$

The plus and minus signs do not imply a complete transfer of an electron from one atom to another. They merely indicate the polarities of the atoms relative to one another and represent the resultant nuclear charge on each atom. The nuclear charge on each atom depends on the displacement of the octet of electrons surrounding each atom as influenced by the directing group X^- or Y^+. The displacement of the electrons, it is believed, may be best expressed by the Lewis–Langmuir theory of electron shift. However, the resultant nuclear charge on each atom, and therefore the relative polarity of each atom, is not governed solely by the displacement of any single pair of electrons but rather by the displacement of the octet electrons surrounding one atom as compared to another.

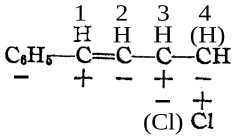
Now let us consider the experimental facts so far obtained in our study of addition reactions to conjugated systems in the light of these electronic structures.

Muskat and Huggins[1a] have studied the chlorination of phenylbutadiene and found that chlorine adds in the 3,4-position to give 1-phenyl-3,4-dichloro-A^1-butene. They further showed that hydrogen chloride could be eliminated from the dichloride to give 1-phenyl-4-chlorobutadiene. These facts find a ready interpretation in the electronic structure proposed. The phenyl radical, the directing group, is usually considered to be relatively electronegative and we should therefore expect the following electronic arrangement in the molecule of phenylbutadiene



$$\begin{array}{ccccccccc} & & H & & H & & H & & H\\ C_6H_5 & - & C & = & C & - & C & = & CH\\ - & & + & & - & & + & & - \end{array}$$

The structure of the dichloride would then be represented as



$$\begin{array}{ccccccccc} & & 1 & & 2 & & 3 & & 4\\ & & H & & H & & H & & (H)\\ C_6H_5 & - & C & = & C & - & C & - & CH\\ - & & + & & - & & + & & -\\ & & & & & & & & - \;\; +\\ & & & & & & & & (Cl)\;Cl \end{array}$$

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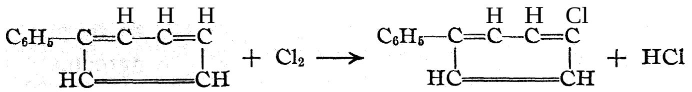
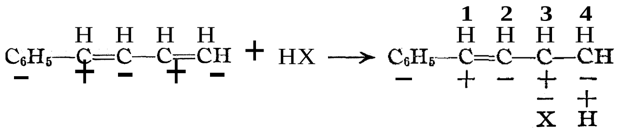
[4] Stieglitz, THIS JOURNAL, 44, 1299 (1922).

[5] Lowry, *J. Chem. Soc.*, 123,822 (1923); Rodebush, *Chem. Reviews*, 5,528 (1928).

in which the 3-chlorine atom would be relatively electronegative with respect to the 4-chlorine atom. In direct accord with this theory, hydrogen chloride is eliminated from the dichloride as indicated by the ( ), to yield 4-chlorophenylbutadiene. This might be regarded as similar to para-substitution of chlorine in diphenyl

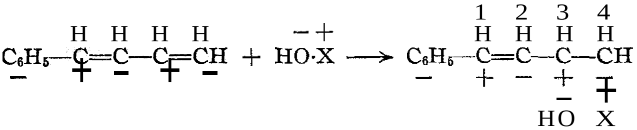


In continuation of this work, Huggins[6] has found that hydrogen chloride and hydrogen bromide add to phenylbutadiene in the 3,4-position, the negative halogen atom going to the relatively positive 3-carbon atom while the positive hydrogen atom attached itself to the relatively negative 4-carbon atom, in direct accord with the electronic structure of the molecule.



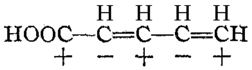
$$\underset{-}{C_6H_5}—\overset{H}{\underset{+}{C}}=\overset{H}{\underset{-}{C}}—\overset{H}{\underset{+}{C}}=\overset{H}{\underset{-}{C}}H + HX \longrightarrow \underset{-}{C_6H_5}—\overset{\overset{1}{H}}{\underset{+}{C}}=\overset{\overset{2}{H}}{\underset{-}{C}}—\overset{\overset{3}{H}}{\underset{\underset{\underset{X}{-}}{+}}{C}}—\overset{\overset{4}{H}}{\underset{\underset{\underset{H}{+}}{-}}{C}}H$$

Grimsley[7] studied the addition of hypochlorous and hypobromous acids to phenylbutadiene and found that these also added in the 3,4-positions. Now, however, the positive halogen atom attached itself to the relatively negative 4-carbon atom, the negative hydroxyl group going to the relatively positive 3-carbon atom.



$$\underset{-}{C_6H_5}—\overset{H}{\underset{+}{C}}=\overset{H}{\underset{-}{C}}—\overset{H}{\underset{+}{C}}=\overset{H}{\underset{-}{C}}H + \overset{-\;+}{HO\cdot X} \longrightarrow \underset{-}{C_6H_5}—\overset{\overset{1}{H}}{\underset{+}{C}}=\overset{\overset{2}{H}}{\underset{-}{C}}—\overset{\overset{3}{H}}{\underset{\underset{\underset{HO}{-}}{+}}{C}}—\overset{\overset{4}{H}}{\underset{\underset{\underset{X}{+}}{-}}{C}}H$$

In the work reported by Muskat, Becker and Lowenstein[1b] on the bromination of vinylacrylic acid and the work reported in this paper on the chlorination of vinylacrylic acid, it was found that both halogens were added in the 3,4-positions. It was also found that hydrogen chloride and hydrogen bromide were eliminated from the vinylacrylic acid dichloride and dibromide to give 3-chloro- and 3-bromovinylacrylic acids, respectively. These experimental facts are in perfect accord with the electronic theory proposed. The carboxyl group, the directing group in this case, is a relatively positive group and we should therefore expect the following electronic orientation in the molecule of vinylacrylic acid



$$\underset{+}{HOOC}—\overset{H}{\underset{-}{C}}=\overset{H}{\underset{+}{C}}—\overset{H}{\underset{-}{C}}=\overset{H}{\underset{+}{C}}H$$

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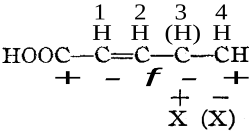
[6] This work is still in progress in this Laboratory.

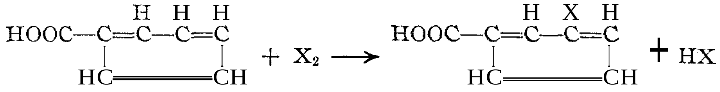
[7] Grimsley, to be published soon.

The dihalide could then be represented as



$$\mathrm{HOOC}\underset{+}{-}\overset{\overset{1}{H}}{\underset{-}{C}}=\overset{\overset{2}{H}}{C}\underset{f}{-}\overset{\overset{3}{(H)}}{\underset{\underset{X}{+}}{C}}\underset{-}{-}\overset{\overset{4}{H}}{\underset{\underset{(X)}{-}}{C}}\underset{+}{H}$$

in which the 4-halogen atom would be relatively electronegative with respect to the 3-chlorine atom and would be expected to be eliminated as hydrogen halide as indicated by the ( ), which is in agreement with the experimentally determined facts. This might be regarded as meta-substitution, similar to the meta-substitution of halogen in benzoic acid.



In studying the addition reactions of conjugated systems we have a marked advantage over the study of similar reactions in the aromatic nucleus for it is possible to isolate the intermediate addition compound prior to its breakdown to the substitution derivative; in the reactions of aromatic compounds, only substitution products can as yet be isolated. The experimental work so far obtained, in the light of the electronic structures postulated, suggests that conjugated systems may act as an intermediate group between the true aromatic and aliphatic groups.

Experimental Part

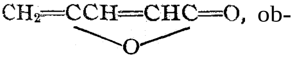
Vinylacrylic Acid **Dichloride.**—To prepare vinylacrylic acid dichloride a stream of dry chlorine was allowed to pass into a chloroform solution of pure vinylacrylic acid. Absorption took place readily and the reaction mixture became warm. When the theoretical quantity of chlorine was absorbed, the reaction product was distilled under reduced pressure. A light yellow oil distilled over at 153° under 10 mm. pressure.

Anal. Calcd. for $C_5H_6O_2Cl_2$: Cl, 41.97. Found: Cl, 41.85, 41.83.

The conditions under which the vinylacrylic acid was chlorinated were varied considerably. Various solvents, such as ligroin, carbon tetrachloride, carbon bisulfide and glacial acetic acid were used besides chloroform, and the temperature was varied from about —20 to about 50°. However, in all cases only one dichloride was obtained regardless of the experimental conditions employed. The dichloride is unstable, particularly toward heat and alkali, and loses hydrogen chloride easily.

The pure vinylacrylic acid dichloride (5 g.), dissolved in chloroform, was subjected to ozonization, and the ozonide thus formed was decomposed with water. To assure complete decomposition it was warmed on the water-bath for a short time. The mixture consisted of aldehydes and acids and was separated by extracting the aqueous solution several times with ether. The aqueous solution was carefully evaporated to dryness and further heated in the oven to 110° for several hours. The residue (2.00 g.) melted at 187°, the melting point of anhydrous oxalic acid. A mixture with pure oxalic acid also melted at 187°. This corresponds to a 75% yield of oxalic acid. The aldehyde portion (from the ether extract) was distilled under reduced pressure. An oil distilled over at 73° under 50 mm. pressure, the boiling point of α,β-dichloropropionic aldehyde. This was further identified by treating with sodium acetate according to the method of Piloty and Stock,[8] which converted the dichloride into a-chloro-acrolein. This distilled over at 40° under 30 mm. pressure, the recorded boiling point of α-chloro-acrolein. This proves that chlorine had added to vinylacrylic acid into the 3,4-position.

Vinylacrylic acid dichloride would not absorb any more chlorine. Even after standing for several days under a pressure of chlorine no addition of chlorine took place. The vinylacrylic acid dichloride was reduced with zinc dust to the original vinylacrylic acid. The yield was low due to polymerization of the vinylacrylic acid during the reduction.

When vinylacrylic acid dichloride was distilled under reduced pressure, decomposition occurred with the liberation of hydrogen chloride. A lower-boiling fraction distilled over which partially solidified on standing. The solid melted at 143° and solidified again at 162". It was identical with the γ-lactone,  $CH_2{=}CCH{=}CHC{=}O$, obtained by the distillation of vinylacrylic acid dibromide.[1b]

Chlorovinylacrylic Acid.—When vinylacrylic acid dichloride was treated with one molar equivalent of sodium hydroxide, the soluble sodium salt of the dichloride was formed. If another molar equivalent of sodium hydroxide was added, the temperature being kept at about 0° during this operation, the dichloride easily lost a molecule of hydrogen chloride and was thus converted into the soluble sodium salt of the monochlorovinylacrylic acid, with an almost theoretical yield. It is of the utmost importance to keep the temperature very low, otherwise the monochloride readily polymerizes The free acid was precipitated as a voluminous crystalline mass on acidifying the alkaline solution with cold dilute acid.

Anal. Calcd. for $C_5H_5O_2Cl$: Cl, 26.76%. Found: Cl, 26.83, 26.81%. It was also titrated with standard sodium hydroxide: 0.3965 g. of sample required 28.1 cc. of 0.1063 N NaOH. Found: mol. wt., 132.7. Calcd. for $C_5H_5O_2Cl$: mol. wt., 132.5.

Chlorovinylacrylic acid is a light yellow, crystalline compound, very soluble in the ordinary organic solvents and rather unstable. It readily polymerizes to a light yellow solid which is insoluble in all ordinary organic solvents with the exception of acetone. Due to its ease of polymerization it is not possible to get a sharp melting point. It melts at about 94°. The structure of the monochloride was established by further chlorinating it to the chlorovinylacrylic acid dichloride and determining the oxidation products of the trichloride formed.

Chlorovinylacrylic Acid Dichloride.—To prepare chlorovinylacrylic acid dichloride a stream of dry chlorine was allowed to pass into a chloroform solution of pure chlorovinylacrylic acid. Absorption took place readily and the reaction mixture became hot. After the theoretical quantity of chlorine was absorbed, the reaction mixture was distilled under reduced pressure. A light yellow oil distilled over at 162° under 8-mm. pressure. On standing it solidified. The solid melted at 132".

Anal. Calcd. for $C_5H_5O_2Cl_3$: Cl, 52.29. Found: Cl, 52.29, 52.09. It was also titrated with standard sodium hydroxide: 0.6947 g. of sample required 31.8 cc. of 0.1063 N NaOH. Found: mol. wt., 205.5. Calcd. for $C_5H_5O_2Cl_3$: mol. wt., 203.4.

The pure chlorovinylacrylic acid dichloride (2.1 g.) was subjected to ozonization and the ozonide thus formed was treated in a manner entirely analogous to that of the dichloride previously described. The acid and aldehyde portions were separated; the acid portion yielded 0.693 g. of calcium oxalate, which corresponds to a 53% yield, while the aldehyde portion was removed as such and distilled under reduced pressure. It distilled over at 63–65° under 45-mm. pressure, the boiling point of α,α,β-trichloropropionic aldehyde. We completely verified the α,α,β-structure of the trichloropropionic aldehyde by oxidizing it to the corresponding α,α,β-trichloropropionic acid with

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[8] Piloty and Stock, Ber., 31, 1385 (1898).

concentrated nitric acid according to the method of Berlande.[9] It melted sharply at 60°. We repeated the preparation of α,α,β-trichloropropionic acid according to Berlande's method and found it to melt at 60° and not at 50–52° as he reports. We analyzed the α,α,β-trichloropropionic acid so prepared to prove its purity.

Anal. Calcd. for $C_3H_3O_2Cl_3$: Cl, 60.0. Found: Cl, 60.37, 60.17.

A mixture of the trichloropropionic acid obtained from the ozonization of chlorovinylacrylic acid dichloride with the synthesized α,α,β-trichloropropionic acid also melted at 60°. It was observed that the acid is very hygroscopic and if allowed to stand in a moist atmosphere for a short time the melting point is materially lowered. This proves beyond any doubt that chlorovinylacrylic acid dichloride has the structure $CH_2ClCCl_2CH{=}CHCOOH$, and therefore the chlorovinylacrylic acid has the structure $CH_2{=}CClCH{=}CHCOOH$.

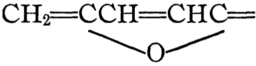
Summary

1. By chlorination of vinylacrylic acid a dichloride is formed whose structure was proved by ozonization to be a 3,4-derivative and not a 1,4-derivative as required by Thiele's theory of addition to conjugated systems.

2. 3,4-Dichloro-Δ^1-pentenic acid loses a molecule of hydrogen chloride to give 3-chlorovinylacrylic acid.

3. 3-Chlorovinylacrylic acid absorbs one molecule of chlorine in the 3,4-position to give 3,3′,4-trichloro-Δ^1-pentenic acid. Its structure was proved by ozonization.

4. On distilling 3,4-dichloro-Δ^1-pentenic acid two molecules of hydrogen chloride are lost and a γ-lactone,



$CH_2{=}CCH{=}CHC{=}O$ (with O bridging) is formed.

5. The melting point of α,α,β-trichloropropionic acid is corrected.

6. An electronic structure for conjugated systems is suggested.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY AND THE BUREAU OF CHEMISTRY AND SOILS]

PHENACYL, PARA-CHLOROPHENACYE AND PARA-BROMOPHENACYL ESTERS OF SOME HIGHER FATTY ACIDS

BY RAYMOND M. HANN, E. EMMET REID AND GEORGE S. JAMIESON

RECEIVED SEPTEMBER 20, 1929 PUBLISHED FEBRUARY 6, 1930

The utilization of phenacyl and para halogen phenacyl esters for the identification and separation of acids has been indicated by Rather and Reid[1] and by Judefind and Reid.[2] The successful employment of these reagents for fruit acids has suggested the possibility of quantitative differentiation of the fatty acids obtained from the saponification of the glycerides contained in fats and vegetable oils. The present accepted analytical procedure for substances of this nature consists in esterify-

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[9] Berlande, Bull. *soc. chim.*, [4] 37, 1385 (1925).

[1] Rather and Reid, THIS JOURNAL, **41,** 75 (1919).

[2] Judefind and Reid, *ibid.*, 42, 1043 (1920).

ing the acids obtained upon saponification, followed by repeated fractionation in vacuo, resaponification and recovery and identification of the free acids. This process, while quantitatively exact, is time consuming and requires close attention and care for its successful completion,

Unfortunately the solubilities of the phenacyl and halogen phenacyl esters of the higher fatty acids are of such an order as to preclude their use in this regard. They are, however, beautiful crystalline compounds which are of value for the establishment of the identity of the higher members of the fatty acid series.

Experimental

The acetophenones and phenacyl bromides were prepared in accordance with the directions of Judefind and Reid. In the preparation of p-chloro-acetophenone an appreciable quantity of *p*-chlorobenzoic acid was isolated as a secondary reaction product. In brominating p-chloro-acetophenone, it was found convenient to dissolve it in twice its weight of glacial acetic acid, add exactly one molecular quantity of bromine, heat gently to decolorization and cool in ice. Pure ω-bromo-*p*-chloro-acetophenone then separated in brilliant plates in quantitative yield.

The general method of procedure adopted for the preparation of the esters was as follows. One gram of acid was weighed out, an amount of normal sodium hydroxide almost sufficient to neutralize the acid was added, and the mixture was boiled with 10 cc. of 95% alcohol until acid to phenolphthalein. An excess of acid is essential to prevent formation of the corresponding phenacyl alcohol, which would contaminate the crystal-

TABLE I

PROPERTIES OF ESTERS OF SOME HIGHER FATTY ACIDS

Ester of	M. p., °C.	Appearance	Soly., g. in 100 cc. of 95% EtOH 20°	25°
		Phenacyl Esters		
Lauric	48–49	Long, soft acicular needles	2.9150	5.3800
Myristic	56	Soft fluffy plates	1.6980	1.7490
Palmitic	63	Brilliant flat scales	0.5136	0.7890
Stearic	69	Dull cottony needles	.2160	.3650
Arachidic	85–86	Soft white powder	.1348	.2660
Lignoceric	87–88	Soft white powder	.1204	.1816
		p-Chlorophenacyl Esters		
Lauric	70	Brilliant scales	0.6060	0.7856
Myristic	76	Brilliant glistening scales	.2472	.3071
Palmitic	82	Brilliant soft needles	.0784	.1020
Stearic	86	Microcrystalline felted needles	.0648	.1000
Arachidic	86	Microcrystalline aggregates	.0100	.0125
Lignoceric	99–100	Microcrystalline powder	.0054	.0072
		p-Bromophenacyl Esters		
Lauric	76	Brilliant scales	0.3832	0.4288
Myristic	81	Brilliant platelets	.1600	.2092
Palmitic	86	Brilliant scales	.0512	.0684
Stearic	90	Brilliant platelets	.0200	.0260
Arachidic	89	Dull microcrystalline aggregates	.0080	.0096
Lignoceric	90–91	Dull microcrystalline powder	.0040	.0072

line fatty acid ester. A molecular proportion of the desired phenacyl or halogen phenacyl bromide was then introduced, and the reaction mixture boiled under a reflux condenser with the addition of sufficient alcohol to keep the reaction product in solution. After being heated for one hour, the flask was cooled, and the separated solid recrystallized from dilute alcohol to constant melting point. Analysis for halogen by the Parr bomb proved the compounds to be the expected esters.

All the phenacyl compounds prepared are colorless crystalline solids, the majority of them exhibiting a marked luster. This property decreases with increase in molecular weight, and a tendency is noted toward decrease in crystal size with increase in molecular weight.

Approximate solubility determinations were made by removing a 25-cc portion of the saturated solution from solutions maintained at 20 and 25° in suitable constant temperature baths and drying to constant weight.

The data which have been accumulated are included in Table I.

Summary

Phenacyl, *p*-chlorophenacyl and *p*-bromophenacyl esters of lauric, myristic, palmitic, stearic, arachidic and lignoceric acids have been prepared and described.

BALTIMORE, MARYLAND
WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

AMMONOLYSIS OF KETONES

BY HAROLD H. STRAIN

RECEIVED SEPTEMBER 23, 1929 PUBLISHED FEBRUARY 6, 1930

In general the ammono ketones[1] have been prepared by the action of ammonia or substituted ammonia on ketones or dihalogen compounds of the formula R_2CX_2, where X represents halogen,[2] and by the reaction of Grignard reagents and the nitriles.[3]

Since the reaction of ammonia with ketones is obviously a reversible

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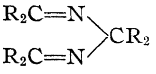
[1] For a discussion of the terms and methods used in this paper see Strain, THIS JOURNAL, 49, 1558 (1927), and the included references to Franklin and his co-workers.

[2] Pauly, Ann., 187,199 (1877); Thomae, *Arch. Pharm.*, 243,395 (1905); Hantzsch and Kraft, *Ber.*, 24, 3516 (1891).

[3] Moureu and Mignonac, Compt. *rend.*, 156, 1801 (1913); ibid., 158, 1395 (1914). Of the three types of ammono ketones which are theoretically possible, only those corresponding to the aldimines and to the ammono aldehyde-acetals are known [Strain, THIS JOURNAL, 50, 2218 (1928)].

$R_2C{=}NH$ Ketimine (known) $R_2C{=}NR$ Ketimine (known)



$$\begin{matrix} R_2C{=}N \\ R_2C{=}N \end{matrix}\!\!>\!CR_2$$ (unknown)

Attempts to prepare the ammono ketones analogous to the hydramides have resulted in the formation of ketisoketimines or other products [Moureu and Mignonac]. Although Thomae [*Archiv. Pharm.*, 243, 373 (1905); *ibid.*, 244, 641 (1906); *ibid.*, 246, 373 (1908)] claims to have prepared an ammono ketone analogous to the hydramides by the action of ammonia on ethyl methyl ketone, his work has been questioned by Traube *[Ber.,*41,777 (1908); *ibid.*, 42,3298 (1909)], who could not duplicate the results.

one if it takes place according to the equation $R_2C{=}O + NH_3 = R_2C{=}NH + H_2O$, the yields of ketimine should be increased by increasing the concentration of the ammonia as, for example, by the use of anhydrous liquid ammonia. As a matter of fact the writer has found that liquid ammonia ammonolyzes aromatic and aromatic-aliphatic ketones to the corresponding ketimine and water.

Removal of the water formed during the ammonolysis should further serve to increase the yield of the ketimine. Attempts to use metallic amides as dehydrating agents resulted in the formation of metallic salts of the ketones. Phosphoric anhydride in contact with liquid ammonia formed a sticky mass which was not active as a dehydrating agent. Calcium chloride also failed to exhibit dehydrating properties in liquid ammonia. Finally, it was found that aluminum chloride was an excellent dehydrating material which could be used in weakly acid solution, that is, in the presence of ammonium salts. By the use of this material in liquid ammonia solution, a number of the ketimines were prepared.

Experimental

Preparation of the Aluminum Chloride.—Aluminum chloride reacts so vigorously with ammonia that the reaction cannot be carried out in the soft glass reaction tubes usually employed in working with liquid ammonia. Accordingly the following procedure was adopted. A rapid stream of ammonia gas was passed over the surface of the aluminum chloride contained in a pyrex test-tube which was supported in a vertical position by means of an iron clamp. The heat of the reaction caused the aluminum salt to melt and as it did so the glass nozzle through which the ammonia was delivered was pushed down into the liquid in order to keep it stirred. When heat ceased to be evolved, the current of ammonia was stopped and the fluid melt poured into a nickel dish where it was allowed to solidify. As soon as it was cool enough to handle, it was pulverized in a mortar, then preserved in a tightly stoppered bottle for future use. When placed in liquid ammonia, the mixture forms a white flocculent mass which settles well.[4]

Ammonolysis of Acetophenone.—Acetophenone was heated with twice its volume of liquid ammonia in a sealed tube at 180° for four hours.[5] After cooling the ammonia was evaporated and the residue dissolved in ether. The ethereal solution was saturated with dry hydrogen chloride, when a white precipitate was obtained. This hydrochloride was filtered off, washed with ether, dissolved in chloroform and reprecipitated with ether. The white crystalline salt thus obtained was slightly hygroscopic, decomposing upon standing in contact with moist air.

Anal. Calcd. for $C_8H_{10}NCl$: Cl, 22.8. Found: Cl, 23.3.

The yield of the acetophenone-imine obtained in the above experiment amounted to 3% of the theoretical quantity. In order to increase this yield the experiment was repeated using a large excess of the aluminum chloride as a dehydrating agent. In this case a yield amounting to **30%** of the theoretical was obtained.[6]

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[4] Although the composition of the compound obtained was not determined, it is probably a mixture of aluminum chloride, ammonium chloride, aluminum chloride with ammonia of crystallization and partly ammonolyzed aluminum chloride.

[5] For method of heating see Blair, THIS JOURNAL, 48, 87 (1926).

[6] No evidence of the compounds reported by Thomae [*Arch. Pharm.*, 244, 641 (1906)] and by Paternò and Maselli [*Gazz. chim. ital.*, 42, I, 65 (1912)] was found.

Ammonolysis of Methyl *p*-Tolyl Ketone.—When methyl *p*-tolyl ketone was ammonolyzed by the method applied to acetophenone, a ketimine hydrochloride was obtained which was very unstable. The analysis of three different preparations showed too high a percentage of chlorine and of nitrogen.

Ammonolysis of Fenchone.—Fenchone was heated at 180° for four hours with four times its volume of anhydrous ammonia and an excess of aluminum chloride. After evaporation of the ammonia the residue was treated as described above for acetophenone, when a white crystalline precipitate of fenchone-imine was obtained. These crystals melted at 274–278° with slight darkening. The melting point of fenchone-imine hydrochloride previously recorded is 278°.[7]

Ammonolysis of Camphor.—Camphor imine was prepared by the method described above and isolated as the hydrochloride. Camphor imine hydrochloride separates from a chloroform–ether solution in long transparent crystals which grow rather slowly. This compound sublimes without decomposing and appears to be identical with the hydrochloride which Mahla and Tiemann obtained by treating camphor imine with hydrogen chloride.[8]

Anal. Calcd. for $C_{10}H_{18}NCl$: Cl, 18.9; N, 7.5. Found: Cl, 19.5, 19.6; N, 6.9.

Reduction of Camphor Imine to Bornylamine.—Camphor imine hydrochloride was suspended in ether, treated with an excess of ammonia and filtered from the precipitated ammonium chloride. The solution was then treated with metallic sodium and finally with alcohol. After the sodium had dissolved, the solution was diluted with water, the ether was evaporated and the residue neutralized with hydrochloric acid. The bornylamine, which is an ammono alcohol, was then precipitated as the picrate, which was recrystallized from water and alcohol. The purified compound melted with decomposition at 241.5° uncorr.[9]

Ammonolysis of Benzophenone.—Benzophenone-imine hydrochloride was prepared by the method used in the preparation of fenchone-imine hydrochloride. The small white crystals which were obtained sublime without decomposing. The yield was 20% of the theoretical.

Anal. Calcd. for $C_{13}H_{12}NCl$: Cl, 16.3; N, 6.4. Found: Cl, 16.4; N, 6.4.[10]

Ammonolysis of Benzil.—Liquid ammonia reacts very slowly with benzil at room temperature forming benzamide and imabenzil, the latter being insoluble in liquid ammonia. Upon heating benzil with liquid ammonia at 200° for two hours, 40% of the ketone is converted into lophine, triphenylimidazole, which is only slightly soluble

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[7] Mahla [*Ber.*, 34, 3777 (1901)] prepared fenchone-imine by the action of nitrous acid on fenchone-oxime.

[8] Mahla and Tiemann, *Ber.*, 29, 2808 (1896).

[9] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1916, Vol. II, p. 116.

[10] Benzophenone-imine was first prepared by Hantzsch and Kraft [*Ber.*, 24, 3517 (1891)], who ammonolyzed benaophenone chloride with urethan, a substituted ammonia. Although Pauly [Ann., 187, 196 (1877)] was unable to ammonolyze benzophenone with ammonia, Thomae [*Arch.* Pharm., 243, 395 (1905)] claims to have prepared benzophenone-imine by the direct ammonolysis of benzophenone with alcoholic ammonia. Later Moureu and Mignonac [*Compt. rend.*, 156, 1801 (1913)] prepared benzophenone-imine by the action of Grignard reagent on acetonitrile, a reaction which is analogous to the addition of Grignard reagent to an acid anhydride. Cornell [THIS JOURNAL, 50, 3314 (1928)] and Smith [unpublished work] have used liquid ammonia to decompose the Grignard addition compound.

in liquid ammonia. These results are similar to those obtained by other workers who used alcoholic ammonia.[11]

The writer is greatly indebted to Dr. E. C. Franklin, who constantly expedited the experimental work with his erudite suggestions.

Summary

A method of ammonolyzing ketones has been developed and applied. The formation of a number of ketimines, which are ketones of the ammonia system as developed by Franklin, is described.

A compound of ammonia and aluminum chloride has been found to be an excellent dehydrating agent in liquid ammonia.

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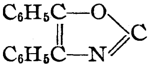
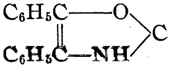
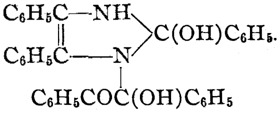
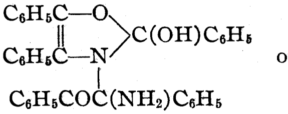
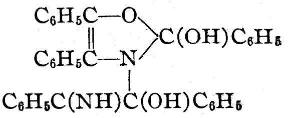
[11] Laurent, *J. prakt. Chem.*, **35, 416 (1845);** Japp and Wynne, *J.* Chem. *Soc.*, **49,** 477 (1886); Henius, Ann., 228, **339 (1885);** Pinner, **Ber., 35, 4138 (1902).**

The formula for benzilam given by Japp and Henius is  that for benzilimide is  while Pinner has suggested the following formula for imabenzil,  However, Henius has shown that imabenzil is easily converted into benzilimide and benzilam, indicating that an oxygen atom may be contained in the ring. Accordingly Pinner's formula might be modified to one of the following



or



[CONTRIBUTION FROM THE RESEARCH AND BIOLOGICAL LABORATORIES OF E. R. SQUIBB AND SONS]

THE RATE OF THERMAL DECOMPOSITION AT 100° OF THE OXYTOCIC PRINCIPLE OF THE POSTERIOR LOBE OF THE PITUITARY GLAND. I. THE EFFECT OF HYDROGEN-ION CONCENTRATION[1]

BY TILLMAN D. GERLOUGH

RECEIVED SEPTEMBER 24, 1929 PUBLISHED FEBRUARY 6, 1930

The rate of thermal decomposition of the oxytocic principle of the posterior lobe of the pituitary body is highly desired information for the manufacturer in selecting proper conditions of extraction and stabilization of pituitary solution and in furnishing data which will assist the investigator in the differentiation of the active principles. Since the advent of this powerful smooth muscle stimulant in obstetrics, very little work has been recorded which will adequately express its stability or rate of thermal decomposition in acid solution despite the varied and voluminous experimentation.

The purpose of this work was to determine the rate of thermal decomposition at 100° of the oxytocic principle of pituitary extracts in acid solution ranging from PH 2.0 to 5.1. These results, for the first time, furnish a complete picture of the effect of hydrogen-ion activity on the rate of thermal decomposition and thereby render more intelligible obscure features in previous experimental work. Such features will be brought out in some detail in the following résumé of the more important experiments on this phase of the pituitary investigations.

According to Guggenheim,[2] Dudley,[3] Abel and Nagayama[4] and Abel, Rouiller and Geiling,[5] the pressor and oxytocic principles are both destroyed when exposed to 1–2 N sodium hydroxide for about two hours at room temperature. The destruction takes place regardless of the method of preparation or purity of the active material.

In strong acid solution the action is not so drastic, therefore the temperature must be elevated to obtain rapid change. Boiling under reflux in 0.5% hydrochloric acid for half an hour abolished the pressor response and destroyed 80% of the total oxytocic activity of the commercial pituitary extracts and the trinitro-aniline salts of "pituitary tartrate" of Abel, Rouiller and Geiling. Under these conditions it appears that the pressor principle is less resistant to change than the oxytocic and, since

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[1] Presented before the joint meeting of the Medicinal and Biological Divisions of the American Chemical Society at St. Louis, Missouri, April, 1928.

[2] Guggenheim, *Biochem. Z.*, 65, 189 (1914).

[3] Dudley, *J. Pharm. Exptl. Therapy*, 14, 295 (1919).

[4] Abel and Nagayama, *ibid.*, 15, 347 (1920).

[5] Abel, Rouiller and Geiling, *ibid.*, 22, 289 (1923).

the active material employed in the various investigations was of such a wide degree of purification, it would seem that purity is not a major factor in regulating the rate of decomposition.

Abel and Nagayama stated that 0.25% hydrochloric acid did not appreciably impair the activity of the commercial extract employed when boiled for one hour, and expressed the opinion that the residual 20% of oxytocic activity remaining in pituitary solutions after treatment with 0.5% hydrochloric acid for half an hour, which appeared to induce maximum reduction in oxytocic value, was due to the formation or the presence of histamine or some histamine-like cleavage product. Dudley, Dale and Dudley, as well as Hanke and Koessler,[6] were unable to accept Abel's explanation and in later investigations Abel and co-workers have concluded that histamine is not a normal constituent of the active material. Dale and Dudley carried the experiment a step farther and found that boiling the active material for six hours in 0.5% hydrochloric acid reduced the oxytocic strength to less than $^1/_{200}$ of its original value. Therefore the simplest explanation is that of incomplete decomposition of the oxytocic principle rather than assigning a special destructive action to 0.5% hydrochloric acid.

While hydrochloric acid in relatively low concentrations quickly destroys the active principle at 100°, acetic acid solutions on the other hand are comparatively stable in wide range of concentrations. According to Stasiak[7] the yield of the oxytocic principle is not impaired by boiling 0.50 g. of acetone defatted posterior lobe in 100 cc. for a "short time" in 0.05 to 6% acetic acid. The same yield was obtained by employing 0.05% (0.0137 N) hydrochloric acid as the extracting solvent. However, with 0.5% hydrochloric acid as the solvent, a loss of 90% of the activity was recorded, which when compared with the data presented herein is indeed a very striking observation because the recorded *P*H's of Stasiak's 0.5% hydrochloric and 6.0% acetic acid extract were of a similar magnitude, which would not allow such a difference in the rate of destruction to occur.[8]

On adjustment of the reaction of an acetic acid extract of the wet posterior lobes to approximately PH 3.0 (colorimetric) Adams[9] found no detectable loss at the end of fifty-five minutes at about 100°. Histamine

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[6] Nanke and Koessler, *J. Biol. Chem.*, *43*, 557 (1920).

[7] Stasiak, *J. Pharm. Exptl. Therap.*, *28*, 1 (1926).

[8] It has been our experience that colorimetric measurements of *P*H of solutions of this type are widely divergent from the values obtained by the hydrogen electrode. A rough comparison to Stasiak values can be seen in Table I. Stasiak determined the PH of his extracts colorimetrically and they ranged from *P*H 2.6 for his 0.50% hydrochloric acid and *P*H **3.4** for his 6% acetic acid extract to PH 7.0 for his 0.05% acetic acid extract.

[9] Adams, J. *Biol. Chem.*, *30*, 235 (1917).

was employed as standard. When the PH was set at 5.0 (colorimetric), the system lost its oxytocic activity very rapidly at the same temperature and the rate of thermal decomposition was found to conform to that calculated for a first-order reaction; 80% of the total activity was lost in fifty-five minutes. Abel and Nagayama claim to have confirmed Adams' finding as to the amount lost in this region of acidity, but direct comparison cannot be made because of the different decomposition conditions. The PH of their pituitary solution was not measured. They further state that when an extract is made just acid to litmus, two hours of boiling does not alter its oxytocic or pressor content.

Experimental

Unless otherwise stated all pituitary solutions studied for the rate of destruction were made by extraction of the acetone dehydrated posterior lobe of pituitary gland of cattle with diluted acetic acid—a procedure employed by many manufacturers and investigators. The method of preparation of the active powder[10] was essentially that of Smith and McClosky[11] with minor modifications. The dried powders represent, consistently, close to 16% of the original weight of fresh posterior lobes.

Extraction of Active Posterior Lobe Powder.—For the study of the rate of thermal decomposition of the oxytocic principle it was desired to have the extracts freed as nearly as possible from inert protein by the simple coagulation that heat affords and still obtain the full oxytocic activity of the powder. The wide divergence of extraction conditions recorded and the absence of definite published data on the PH at which the heat coagulable protein is most effectively removed, made it necessary to subject this step to a close examination to insure reproducibility. Extractions were made with varying concentrations of acetic acid, acetic acid in saline salt and hydrochloric acid, and analyses made of each solution for total nitrogen and the nitrogen in the filtrate after precipitation with tungstic acid. The oxytocic value of the solution extracted at PH 3.2 ± 0.2 and 4.4 ± 0.2, respectively, for each type of extraction was also determined.

The actual extraction was conducted as follows: 1.00 g. of finely divided active powder, which had been sifted through a 40-mesh sieve, was placed in suitable hard glass flasks. Part of the desired extraction solution was added and the mixture allowed to stand for ten to fifteen minutes with frequent agitation. The remainder of the 100 cc. was then added, the flask plugged with cotton and placed in a boiling water-bath for twelve to fourteen minutes, then withdrawn, filtered or centrifuged and the extract analyzed. The final temperature reached was 96–98°.

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[10] Aldrich, THIS JOURNAL, 37, 203 (1915).

[11] Smith and McClosky, U. S. P. H. Bull. Hyg. Lab. No. 138 (1924).

The relationship between the concentration of the extracting acid[12] and the resulting PH and nitrogenous matter of the extracts is shown in Table I and the data are correlated graphically in Fig. 1. The percentage of acetic acid is given in the first column of Table I for convenient comparison with the work of other investigators. Column 5 gives the mg. of nitrogen per cc. found in the filtrate after precipitation of the extract with tungstic acid by the method of Folin and Wu.[13] These values are fairly constant and not influenced by the PH of extraction. Considerable

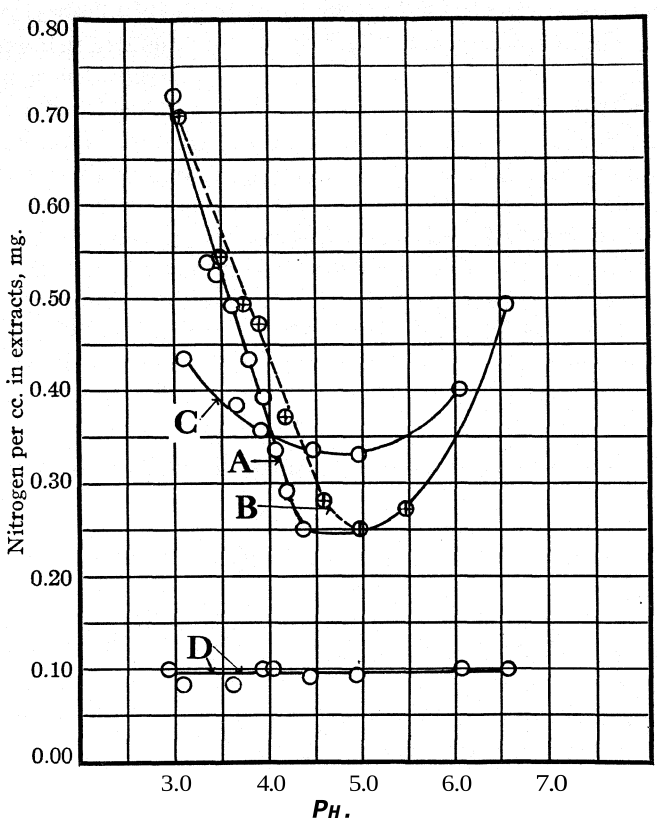

Fig. 1.—Extraction of nitrogenous material from desiccated posterior lobe No. 10941 by (A) acetic acid, (B) hydrochloric acid and (C) No. E9984 by acetic acid in 0.85% sodium chloride. (D) Extracts after precipitation with tungstic acid.

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[12] For a given concentration of acid the resulting PH of the extract is a function of the quantity or concentration of the powder extracted. For example, 4.00, 2.00, 1.00, 0.400, 0.200 and 0.100 g. of powder No. 9767 were extracted as above with 100 cc. of 0.20% acetic acid for twenty minutes and the resulting *PH*'s of the extracts at 25° were, respectively, 4.54, 4.24, 3.89, 3.57, 3.42 and 3.28.

[13] Folin and Wu, *J. Biol. Chem.*, **38,** 81 (1919).

oxytocic activity, about 30–40% of the total, was found in the tungstic acid filtrate of extracts previously extracted at *PH* 4.3. This point was not investigated on extracts prepared at other acidities. Column 6 gives mg. of nitrogen per cc. after the reaction of the more acid extract was adjusted back at room temperature to the "isoelectric zone." The nitrogen values are not entirely reduced to the level found after coagulation at elevated temperature. The other columns are self-explanatory.

Under the condition of extraction outlined practically the same oxytocic value was obtained for the extracts of *PH* 3.2 ± 0.2 as for those extracted at *PH* 4.4 ± 0.2 regardless of the type of solvent. Comparison on a weight basis with the U. S. P. X. Standard Powdered Pituitary, which is referred to as 100% activity, showed our experimental solutions to be on an average of 50–60% activity. Selection of optimum extraction conditions with respect to the elimination of excessive inert protein readily can be judged by inspection of Fig. 1. Keeping in mind that the rate of decomposition is rapid enough at 100° to produce considerable loss if the reaction is *PH* 5.0 to 6.0, then losses can be minimized and maximum coagulation of inert protein still obtained if the reaction of the resulting extract is PH 4.4 ± 0.2 with acetic acid. The final temperature as previously mentioned was 96–98'. The zone of maximum coagulation in the case of hydrochloric acid was approximately *PH* 4.7–5.2. In this region of acidity the rate of decomposition becomes a more important factor and is apt to produce measurable losses if the extracting system is boiled at 100°, 0.85% sodium chloride in acetic acid holds too much protein in solution to yield the desired condition although its coagulation zone is broad enough to allow easily filtered extracts to be made in more acid solution.

The extraction results as shown in Table I were reproduced on a number of other samples of acetone defatted posterior lobe.

Method of Conducting Destruction.—The total acetic acid concentration of the extracts was increased after filtration to 0.20% and further adjustments of *PH* were made with hydrochloric acid or sodium hydroxide. The hydrogen-ion activity was then determined by the hydrogen electrode at 25°. The solutions were sealed in special 1.0-cc. hard glass ampules and placed in streaming steam, the temperature of which was 99.8–100°, and withdrawn at times designated in the tables. The *PH* was again measured and it did not deviate after any heating period more than 0.10 unit of PH from the original value. Assay of oxytocic strength was promptly made—particularly on those solutions whose *PH* was close to 2.0 or 5.0—by checking against the control solution. The control solution was finally assayed against the U. S. P. X. standard extract. All controls and ampules were properly preserved or sterilized and held at ice-box temperature.

TABLE I

EXTRACTION OF NITROGENOUS MATERIAL FROM 1.00 G. OF DESICCATED POSTERIOR LOBE POWDER WITH ACETIC AND HYDROCHLORIC ACIDS

HAc, %	HAc, mole/liter	PH of extr	Total nitrogen, mg./cc.	Nitrogen in filt. after pptn. with tungstic acid, mg./cc.	Nitrogen in filt. after adjust. of extr. to PH 5.0, mg./cc.
A. Acetic acid: Powder E-9984					
0.00	0.000	6.58	0.49	0.10	..
.025	.0042	4.82	.28	.10	..
.05	.0083	4.46	.27	.11	..
.10	.0166	4.17	.28	.10	..
.25	.0416	3.77	.43	.08	0.28
.40	.0666	3.58	.48	.09	.37
.60	.1000	3.50	.52	.10	.37
.60 + 1 cc. of N HCl		3.00	.72	.10	.40
Powder No. 10941					
0.070	0.0116	4.35	0.25	..	..
.100	.0166	4.22	.29	..	..
.200	.0333	3.94	.39	..	..
.300	.0499	3.79	.43	..	..
.500	.0833	3.62	.49	..	..
.750	.125	3.48	.53	..	..
1.000	.166	3.38	.54	..	..
B. Acetic acid in 0.85% sodium chloride: Powder E-9984					
0.00	0.0000	6.09	0.40	0.10	..
.024	.0040	4.93	.33	.09	..
.050	.0083	4.49	.34	.09	..
.100	.0166	4.06	.34	.10	..
.200	.0333	3.90	.36	.10	..
.350	.0580	3.69	.38	.08	..
.600	.100	3.10	.43	.09	.39
.60 + 1 cc. of N HCl		2.94	.54	.10	.46
C. Extraction of active powder by hydrochloric acid: Powder 10941					
	(HCl)				
	0.0020	5.48	0.27	..	..
	.0030	4.92	.25	..	
	.0040	4.56	.28	..	0.30
	.0050	4.14	.37	..	.36
	.0060	3.87	.47	..	.35
	.0070	3.68	.49	..	.35
	.0085	3.48	.54	..	.35
	.0110	3.08	.69	..	.50
Powder E-9984					
	0.0035	4.55	0.27	..	..
	.0050	4.30	.41	0.08	0.30
	.0070	3.60	.50	.08	.33
	.0100	3.18	.69	.10	.37

The Oxytocic Assay.—The method of assaying the oxytocic strength was essentially that of Dale and Laidlaw,[14] which we have used successfully for a number of years. Needless to say, it required several months of

TABLE II

RATE OF DESTRUCTION OF THE OXYTOCIC PRINCIPLE OF THE POSTERIOR LOBE

t, min.	$a - x$	$K = 1/t\ 2.3 \log a/(a - x)$	t, min	$a - x$	$K = 1/t\ 2.3 \log a/(a - x)$
	D-8889—PH 2.03			0-1224—PH 3.06	
0	1.00		0	1.00	
60	0.82	0.0033	240	0.86	0.00063
120	.67	.0033	480	.76	.00057
240	.40	.0038	1440	.47	.00052
480	.18	.0036			
960	.05	.0031		Av.	0.00057
				10122—PH 3 25	
	Av.	0.0034	0	1.00	
	C-8889—PH 2.26		420	0.80	0.00053
0	1.00		960	.57	.00058
120	0.76	0.0023			
240	.65	.0018		Av.	0.00055
480	.43	.0018		E-8889—PH 3.82	
960	.19	.0017	0	1.00	
1500	.04 (about)	.0021[a]	60	0.91	0.0016
			120	.86	.0012
	Av.	0.0019	240	.71	.0014
	9188—PH 2.41		480	.53	.0013
0	1.00		960	.33	.0011
60	0.91	0.0016	1500	.19	.0011
180	.80	.0012			
300	.65	.0014		Av.	0.0013
540	.49	.0013		B-8889—PH 4.32	
1020	.26	.0013	0	1.00	
			60	0.78	0.0041
	Av.	0.0014	120	.67	.0033
	E-8889—PH 2.72		240	.41	.0037
0	1.00		480	.17	.0035
120	0.93	0.00060	960	.05	.0031
240	.86	.00063			
480	.71	.00071		Av.	.0035
960	.50	.00072		A-8889—PH 5.11	
1500	.35	.00070	0	1.00	
			35	0.65	0.012
	Av.	0.00067	60	.50	.011
			120	.28	.011
			240	.09	.010
				Av.	0.011

[a] Not *included* in *average*.

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[14] *Dale and* Laidlaw, *J. Pharm. Exptl. Therap*, 4, 75 (1912).

TABLE III

SUMMARY OF THE RATE OF DESTRUCTION OF OXYTOCIC PRINCIPLE IN PITUITARY SOLUTION[a]

Serial no.	PH	K_{100}	Log $1/K$	Remarks
D-8889	2.03	0.034	2.47	
C-8889	2.26	.0019	2.72	
9188	2.41	.0014	2.85	Contains 0.5% of phenol
E-8889	2.72	.00067	3.17	
O-1224[b]	3.06	.00057	3.24	
10122[c]	3.25	.00055	3.26	Contains 0.5% of phenol
F-8889	3.82	.0013	2.88	
B-8889	4.32	.0035	2.46	
A-8889	5.11	.0110	1.96	
8902–10	4.92	.0067	2.17	$a-x = 0.20$ in 240 minutes
8902–9	4.21	.0028	2.55	$a-x = 0.51$ in 240 minutes
8902–11	3.57	.00097	3.01	$a-x = 0.79$ in 240 minutes
8902–13	3.21	.00050	3.31	$a-x = 0.88$ in 240 minutes
8902-C	3.15	.00058	3.23	$a-x = 0.87$ in 240 minutes
8902–14	2.64	.00093	3.03	$a-x = 0.80$ in 240 minutes
8902–15	2.15	.0037	2.43	$a-x = 0.41$ in 240 minutes

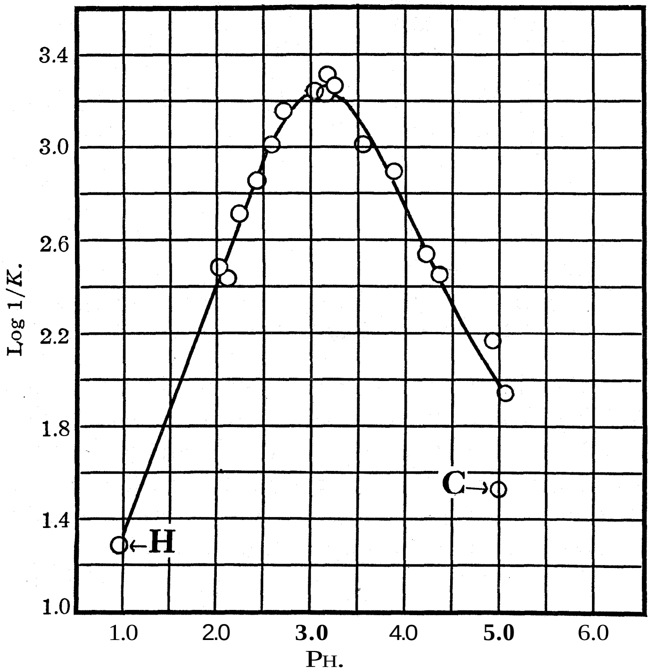
[a] Initial strength of all solutions, 55% U. S. P. X. [b] Method of preparation unknown, 110 U. S. P. X. [c] Initial strength, 100% U. S. P. X.

continuous testing to obtain the results shown in this paper and it is obvious that the actual kymographic records of contractions are too voluminous to be incorporated herein. As a general procedure the equivalent dose for each solution was determined two or three times against the control or standard. Several uterus muscles were usually required. The oxytocic strength was averaged and rounded to the nearest percentage. Under favorable conditions the oxytocic assay method is capable of a relative variation of less than 10%.

Experimental Results

The oxytocic activity remaining after time, t, in minutes has elapsed is expressed as $a - x$ in Tables II and III. K_{100} is the constant for the rate of thermal decomposition at 100° at a given PH and is calculated from the equation $K = (1/t\ 2.3 \log [a/a - x])$. The equation is that of a first order reaction and the terms have their customary significance. A is unity for the control solution. For convenience in plotting Fig. 2, K_{100} is expressed as log $1/k$, increase of which means greater stability. Maximum stability occurs in a rather limited range of PH, *viz.*, 3.0–3.4, or, more specifically stated, pituitary solutions adjusted to PH 3.0–3.4 at 25° are most stable at 100°. These results were again checked on another series of solutions made from a different powder by determining the activity left after 4.0 hours of heating at 100° and the data recorded in Table III under Serial No. 8902–9, etc. All solutions of the series contained 0.01

M NaH_2PO_4 in addition to the usual buffer, acetic acid. The sharp maximum again clearly showed the regulation of the rate of decomposition by the hydrogen-ion concentration. This is the essential factor of stability of pituitary extracts and it is important to note that the oxytocic principle of extracts made from three active powders (see solutions under serial numbers of 8889, 8902, 10122 and a commercial preparation 0–1244 of unknown history and purification) have practically the same stability at PH 3.0-3.4.



H, Dale and Dudley, Abel and co-workers; C, Adams.

Fig. 2.—Rate of thermal decomposition of the oxytocic principle.

Other factors such as the presence of inert protein material and salts may perhaps alter the rate of decomposition somewhat, although definite information on these factors is not available. We have fragmentary evidence that 0.5 N sodium chloride accelerates at PH 3.2 the rate of decomposition of the oxytocic principle of the extracts.

0.5 Per cent. phenol evidently does not produce any detectable alteration in the rate of destruction. Chloretone (trichloro-*tert.*-butyl alcohol, CCl_3-$COHCH_3CH_3$), however, causes a marked change in the rate as a consequence of formation of free hydrochloric acid from chloretone.[15] To

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[15] Chloretone solutions saturated at room temperature were found to be completely hydrolyzed in seventy-two hours at 100° in sealed glass tubes.

illustrate this point: a pituitary solution (about P_H 3.3) which assayed 80% of U. S. P. X. strength and contained 0.5% of chloretone and 0.16 mg. of nitrogen per cc. was heated in sealed ampules for seven and sixteen hours. The oxytocic activity remaining was 53 and 38%, respectively. During the decomposition the reaction of the solution heated for sixteen hours was now found to be about P_H 2.0. As a check, solution No. 10122 (See Table II) was run simultaneously.

Solutions with the initial oxytocic strength of 55,100 and 110% U. S. P. X. showed the rate of destruction to be independent of concentration or oxytocic strength at a given P_H. This, of course, was predicted if the order of reaction is correct. The same relationship holds for solutions refluxed in 0.5% hydrochloric acid for 0.50 hour in the experiments described by Abel and co-workers and by Dale and Dudley and others. Under these conditions 20% of the total oxytocic strength was still present regardless of the original strength or purity of their preparations.[16] Since there is no indication at present that the order of reaction changes when decomposition occurs in hydrochloric acid, then the constant for the rate of change in 0.50% hydrochloric acid is computed as 0.054 and log $1/k = 1.28$. The P_H of the acid at 25° is close to 0.95. These values conform nicely to the data of this paper.

On the basis of hydrogen-ion activity these data explain the rapid destruction in relatively low concentrations of hydrochloric acid and relatively high degree of stability in a weak acid like acetic in concentration as high as 6.0%.[7,17] Sharp breaks in the degree of stability, like those shown by Abel and Nagayama, are not to be expected. Several hours of heating at 100° is sometimes necessary to destroy sufficient active material to produce easily detectable differences. This is probably the situation in Adams' work conducted at approximately P_H 3.0 (colorimetric), in which he found no detectable loss after fifty-five minutes of heating at 100°.

In conclusion this paper suggests the importance of investigating the rate of destruction of the pressor principle. Although it seems settled that the rate of decomposition is faster for the pressor principle than the oxytocic in 0.50% hydrochloric acid and at P_H 6.0,[15] yet these data are not sufficient to venture a prediction as to its stability at intermediary acidities or give an indication of the P_H of maximum stability of the pressor principle.

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[16] It would be interesting to note the extent to which the rate of thermal decomposition is governed by the removal of inert material. This study has heretofore been handicapped by the lack of suitable methods of purification which would insure reproducible material. A feasible method for purification and practically complete separation of the oxytocic and pressor principle is now available through the splendid work of Kamm and co-workers, THIS JOURNAL, **50,** 573 (1928).

[17] Tate, *Pharm.* J. (London), 106, 486 (1921).

Summary

1. The rate of thermal decomposition at 100° of the oxytocic principle of pituitary solution has been determined between P_H 2.0 and 5.1.

2. The rate conforms to that calculated for a first order reaction.

3. A sharp reproducible maximum in stability occurs at P_H 3.0–3.4.

4. Details of the simple extraction process have been worked out for the oxytocic principle only. Maximum coagulation occurs at P_H 4.8–5.0. The zone is wide enough to allow routine and effective extraction at P_H 4.2–4.5 under the conditions described.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF TRINITY COLLEGE, CONNECTICUT, AND THE UNIVERSITY OF MISSISSIPPI]

THE REDUCTION OF MONONITROPYROCATECHOLS[1]

BY JOHN E. FOGLESONG AND I. L. NEWELL

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The results presented in this communication represent an outgrowth of a project to prepare monohalogen derivatives of pyrocatechol by nitration, reduction, diazotization and substitution. The nitration of pyrocatechol results in two isomeric mononitro compounds

$$1,2\text{-}(OH)_2\text{-}C_6H_3\text{-}NO_2\text{-}3 \quad \text{and} \quad 1,2\text{-}(OH)_2\text{-}C_6H_3\text{-}NO_2\text{-}4$$

which upon reduction form the corresponding amines. It can be readily seen that this offers the possibility of obtaining certain pyrocatechols substituted in either the 3- or 4-position. Since 3-aminopyrocatechol had not been prepared, it seemed profitable to study it and some related compounds in detail.

In their work on aromatic amines, Jacobs and Heidelberger[2] prepared 4-aminopyrocatecholhydrobromide, 4-aminopyrocatechol, and several compounds derived from them. They arrived at the hydrobromide through sulfanilic acid, *p*-sulfophenylazoguaiacol, 4-aminoguaiacol, and finally 4-aminopyrocatechol hydrobromide by demethylation with hydrobromic acid.

Our work will show that the same results can be obtained easily and in good yield by the direct nitration of pyrocatechol, the separation of the isomers and subsequent reduction.

Nitration of Pyrocatechol.—Pyrocatechol was first nitrated by Benedikt[3] using a nitration mixture of potassium nitrate and sulfuric acid. It was not recognized that two isomers were formed and the melting point

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[1] Part of the material of this paper has been taken from a thesis submitted by I. L. Newell to the faculty of Trinity College (Connecticut), in partial fulfilment of the requirements for the degree of Master of Science.

[2] Jacobs and Heidelberger. THIS JOURNAL, 41, 467 (1919).

[3] Benedikt, *Ber.*, 11, 362 (1878).

indicates that the final product was a mixture. The method was improved by Weselsky and Benedikt,[4] using fuming nitric acid on pyrocatechol in ether solution. The isomers were separated by steam distillation, the 3-nitro compound being volatile, while the 4-nitro compound is not. Their conclusions as to the position of the nitro groups were based entirely on the analogous behavior of o- and *p*-nitrophenols under steam distillation. However, the constitution of these compounds has been determined by Cousin[5] and by Moureu.[6] Vermeulen[7] found that the 3-nitropyrocatechol could be dissolved out of the nitration mixture by means of petroleum ether, thus eliminating the long steam distillation.

In our work pyrocatechol was nitrated in ether solution as indicated above, and the residue prepared for extraction according to Vermeulen's method. However, we found that 3-nitropyrocatechol is only very slightly soluble in petroleum ether, but the extraction can be carried out with a petroleum distillate boiling at about 100°. Practical heptane from petroleum (Eastman) is well suited for this purpose. On cooling the boiling heptane solution in ice water, 3-nitropyrocatechol is deposited. Several extractions are necessary to remove the major portion. The crude 4-nitropyrocatechol is next subjected to steam distillation until the distillate is nearly colorless. The residual solution is then evaporated to dryness and the residue extracted with boiling xylene.[4] After recrystallization from 20% alcohol the melting points of the two isomers correspond to those recorded.

Several nitrations have shown that the yield is about 80% of the theoretical; 5–8% of this yield is 3-nitropyrocatechol.

Benedikt noticed that alkalies impart a purple color to a solution of nitropyrocatechols. The colorimetric properties of these compounds have proved interesting and are being further investigated in this Laboratory.

Experimental Part

The Reduction of Nitropyrocatechols.—Benedikt reduced nitropyrocatechols to the amino hydrochlorides, but was unable to obtain the free amines. If strong bases are used to form the free amine, the latter is destroyed by oxidation in the air. The reduction can be carried out in the usual manner with tin and hydrochloric or hydrobromic acid, tin precipitated with hydrogen sulfide, and the solution evaporated under reduced pressure.

3-Aminopyrocatechol Hydrochloride.—The almost colorless crystals resulting from the evaporation were recrystallized from 85% alcohol, to which a little hydrochloric acid had been added. On cooling in the ice box, the hydrochloride separated as slightly gray, flat needles or narrow plates. It darkened somewhat at 160° and melted at 196–202°. It is readily soluble in water, giving a faint violet tinge, readily soluble in alcohol

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[4] Weselsky and Benedikt, *Monatsh.*, 3, **386 (1882).**

[5] Cousin, **Ann.** *chim.*, [7] **13,498 (1898).**

[6] Moureu, *Bull. soc. chim.*, [3] **15,649 (1896);** *Compt.* **rend., 122,477 (1896).**

[7] **Vermeulen,** *Rec. trav. chim.*, **25, 23 (1903).**

and ether, but less so in benzene or petroleum ether. Ferric chloride gives a deep violet color.

Anal. (Kjeldahl). Subs., 0.3872: 16.05 cc. of 0.1956 *N* HCl. Calcd. for C_6H_7N-HCl: N, 8.67. Found: N, 8.78.

3-Aminopyrocatechol.—The free amine was prepared by treating a concentrated aqueous solution of the hydrochloride with a saturated solution of sodium bicarbonate from a dropping funnel. The entire operation, as well as the subsequent filtration and washing with ice water, was carried out in an atmosphere of carbon dioxide to prevent oxidation[2] The base crystallizes in nearly colorless prisms which darken in the air. It is readily soluble in water and alcohol, but less so in benzene. After protracted drying in a vacuum desiccator over calcium chloride, it melted at 120–122° with decomposition.

Anal. (Kjeldahl). Subs., 0.4475: 18.36 cc. of 0.1956 N HCl. Calcd. for $C_6H_7O_2N$: N, 11.21. Found: N, 11.27.

4-Aminopyrocatechol hydrobromide and 4-aminopyrocatechol were prepared in an analogous manner and found to be identical with those prepared by Jacobs and Heidelberger.

Diacetyl-3-acetaminopyrocatechol.—Ten grams of 3-aminopyrocatechol hydrochloride was mixed with 5 g. of fused sodium acetate and boiled for one hour with an excess of acetic anhydride. The resulting mixture was poured into water and neutralized with dilute sodium carbonate solution. The crude triacetate was extracted with chloroform. After distillation of the chloroform, the residue was crystallized from boiling toluene, to which norit had been added to get rid of a pink color. It was recrystallized from 20% alcohol. The yield was 10 g. of glistening white, pointed blades melting sharply at 97°. It is readily soluble in alcohol and chloroform, slightly soluble in ether, cold water or toluene but readily soluble in the hot solvents.

Anal. (Kjeldahl). Subs., 0.5006: 9.68 cc. of 0.2035 N HCl. Calcd. for $C_{12}H_{13}NO_5$: N, 5.55. Found: N, 5.50.

The isomeric diacetyl-4-acetaminopyrocatechol has been prepared by Kehrmann and Hoehn[8] and the two compounds agree very closely in their properties.

Diacetyl **3-Aminopyrocatechol.**—The methods used by Jacobs and Heidelberger[2] for the 4-amino isomer readily yielded this compound. Ten grams of 3-aminopyrocatechol hydrochloride was dissolved in 40 cc. of water and 46 cc. of saturated sodium acetate solution added. Eight cc. of acetic anhydride was added, and on shaking the compound was deposited. A further yield was obtained by saturating the filtrate with solid sodium acetate and adding 5 cc. more acetic anhydride. The yield was 10 g. of crude material. It was purified by crystallization from 50% alcohol after decolorization with norit and is slightly soluble in cold water or 50% alcohol, but readily soluble in the boiling reagents. It forms irregular hexagonal plates melting at 167–168° which are grayish white in color and glisten in the light. An aqueous suspension, when acidified with acetic acid and treated with sodium nitrite solution, forms a nitroso compound which crystallizes as golden yellow plates when the solution is chilled and agitated. The nitroso compound dissolves in alkalies with a brown to red color. The properties of the diacetyl3-aminopyrocatechol thus agree very closely with the 4-amino isomer.

Anal. of the diacetate (Kjeldahl). Subs., 0.4856: 11.64 cc. of 0.2035 N HCl. Calcd. for $C_{10}H_{11}O_4N$: N, 6.70. Found: N, 6.83.

3-Acetaminopyrocatechol.—This compound can be prepared by treating 3-aminopyrocatechol hydrochloride in 50% acetic acid solution with 1.2 moles of acetic anhy-

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[8] Kehrmann and Hoehn, *Helv. Chim. Acta*, 8,218 (1925).

dride. The solution is warmed slightly and allowed to stand for twenty-four hours. It is then evaporated to dryness under reduced pressure and the residue extracted with ether. The ether is removed, the crude material dissolved in chloroform and precipitated by the addition of petroleum ether.

The acetamino compound can be more conveniently prepared from the triacetate by partial hydrolysis according to a method devised by Kehrmann and Hoehn.[8] The triacetate is added to 33% sodium hydroxide solution, and goes into solution with evolution of heat. In a few minutes the acetyl groups are hydrolyzed, after which the solution is cooled to 0° and neutralized with sulfuric acid. The acetamino compound is extracted with ether and purified as before. The yield is not good by either method of preparation. It is easily soluble in water, but slightly soluble in the hot solutions. It is insoluble in petroleum ether. From toluene or chloroform it forms white microscopic blades, melting at 124–125°. From water it forms regular tetrahedra, but crystallization is attended by gum formation. The 3-acetaminopyrocatechol forms a gray lead salt and gives an olive green color with ferric chloride. In contact with the air the aqueous solution assumes a red color which is probably due to quinone formation, since the color is discharged by sulfur dioxide.

Anal. (Kjeldahl). Subs., 0.2074: 5.96 cc. of 0.2035 *N* HCl. Calcd. for $C_8H_9O_3N$: N, 8.38. Found: 8.21.

The isomeric 4-acetaminopyrocatechol was prepared intermediately by Kehrmann and Hoehn but not isolated.

Summary

Pyrocatechol has been nitrated and the process for the separation of the isomers definitely established. The corresponding amines have been prepared by direct reduction, and 3-aminopyrocatechol and some compounds arising from it have been described. The procedure for the preparation of other pyrocatechols substituted in either the 3- or 4-position has thus been simplified. Further work along this line is in progress in this Laboratory.

UNIVERSITY, MISSISSIPPI

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 616]

THE CHEMISTRY OF THE ACYL PARA-QUINONES. A CONTRIBUTION TO THE SOLUTION OF THE "PECHMANN DYES" PROBLEM[1]

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By the action of acetic anhydride upon β-benzoylacrylic acid, and some of its homologs, von Pechmann[3] obtained, in 1882, deeply colored products whose chemical constitution he did not ascertain. These products, which have been known since as "Pechmann Dyes," were studied twenty-four years later by Kozniewski and Marchlewski,[4] who assigned to them the

[1] Presented in abstract before the Division of Organic Chemistry, at the St. Louis Meeting of the American Chemical Society, April, 1928.

[2] Recently Lydia C. Roberts Graduate Fellow at Columbia University.

[3] Von Pechmann, *Ber.*, 15, 885 (1882).

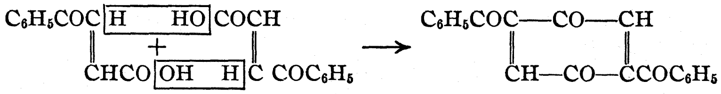
[4] Kozniewski and Marchlewski, Bull. *acad. sci. Cracow,* 81 (1906).

structures of diaroyl p-quinones. In 1924 Bogert and Ritter[5] attacked the problem and, as the result of their experimental work, came to the conclusion that these compounds did not possess the constitution ascribed to them by Kozniewski and Marchlewski, but that the simplest Pechmann Dye at least was probably the trans-dilactone of diphenacylmaleic acid.

Although the evidence upon which this conclusion was based seemed good, it was decided to follow the matter further by the study of diaroyl p-quinones prepared in other ways. These syntheses and studies are recorded in the following pages, and support the contention that the Pechmann Dyes do not belong to this class.

At the time this research was begun, aside from the Pechmann Dyes, we were unable to find any mention of acylated p-quinones in the literature, and there was therefore the added incentive of contributing something to fill this gap.

Kozniewski and Marchlewski explained the formation of the simplest Pechmann Dye thus



$$\begin{array}{l} C_6H_5COC\boxed{H \quad HO}COCH \\ \| \qquad + \qquad \| \\ CHCO\boxed{OH \quad H}C\ COC_6H_5 \end{array} \longrightarrow \begin{array}{l} C_6H_5COC—CO—CH \\ \| \qquad\qquad \| \\ CH—CO—CCOC_6H_5 \end{array}$$

The crux of the problem was, therefore, the synthesis of 2,5-dibenzoyl-p-benzoquinone by some other method and the determination of its identity or non-identity with this Pechmann Dye. The steps in this synthesis are shown on the Flow Diagram herewith and although we have not succeeded in proving conclusively that the two benzoyl groups are in the para position to each other, the evidence is all in favor of such an assumption. We have at least demonstrated that the dibenzoylbenzoquinone synthesized in this way exhibits properties which are quite different from those of the Pechmann Dye.

Since the simplest method of preparing such acylated quinones was obviously the oxidation of the corresponding acylated hydroquinones, it became necessary to develop improved methods for the synthesis of these latter, for the methods already in the literature were not very satisfactory.

The acylation of dihydric phenols has been studied more frequently and more successfully in the case of resorcinol than with either of its isomers. Methods which proved satisfactory when applied to resorcinol have given either much reduced yields or no yields at all when applied to hydroquinone, due largely to the much greater sensitivity and reactivity of this isomer.

The monobenzoylhydroquinone was obtained in good yields by starting with the dimethyl ether of hydroquinone, introducing the benzoyl group by a Friedel–Crafts reaction and demethylating in two steps.

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[5] Bogert and Ritter, (a) THIS JOURNAL, 46, 2871 (1924); (b) Proc. *Nat. Acad. Sci.*, 10, 363 (1924).

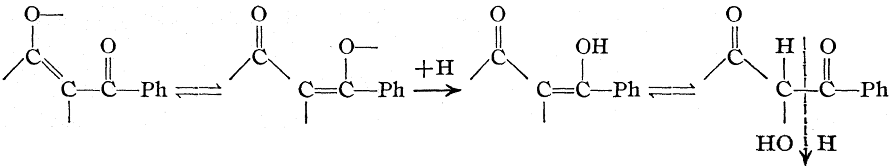
Dibenzoylhydroquinone was secured from hydroquinone dibenzoate, benzoyl chloride and anhydrous aluminum chloride, at temperatures near 200°, by a modification of the process of Doebner and Wolff.[6] The failure of the experiments designed to establish the location of the benzoyl groups was due in part to the difficulty encountered in reducing the benzoyl groups to the corresponding hydrols, and in part to our inability to obtain a pure dibromo substitution product of the diacylated hydroquinone.

Both mono- and dibenzoylhydroquinones were oxidized smoothly to the corresponding acylated quinones by cold chromic acid mixture.

It has been shown that a benzoyl group adjacent to a methoxyl renders the latter much less stable to demethylating agents. Thus the partial demethylation of monobenzoylhydroquinone dimethyl ether, as carried out by Kauffmann and Grombach,[7] was shown by Auwers and Rietz[8] to be the 2-hydroxy-5-methoxybenzophenone, with which conclusion Kauffmann agreed, in a private communication,[8] after showing that one of the methoxyl groups in nitrohydroquinone was more readily demethylated than the other. Our own results are in harmony with these, for both of the methyl groups were easily removed from dibenzoyl hydroquinone dimethyl ether, and this is therefore an additional support of the assumption that the two benzoyl groups were not adjacent to the same methoxyl in our product.

Comparative oxidation and reduction reactions carried out with these benzoylated hydroquinones and quinones showed quite clearly that the monobenzoylhydroquinone was more rapidly oxidized, in either acid or alkaline solution than the dibenzoyl and that, as might have been expected, the dibenzoyl quinone was the more rapidly reduced. Similarly, the dibenzoylhydroxyhydroquinone was less rapidly oxidized than the monobenzoyl.

In the attempted reduction of dibenzoylhydroquinone to the dihydrol by the action of 3% sodium amalgam upon its suspension in water, a strong odor of benzaldehyde was soon apparent. The blood-red color which always developed when the yellow crystals of either the mono- or dibenzoylhydroquinone were dissolved in caustic alkali, suggests a tautomeric change, analogous to that occurring in the case of β-diketones, which perhaps may be formulated thus



(A) yellow (B) blood-red (C) (D)

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[6] Doebner and Wolff, Ber., 12, 661 (1879).

[7] Kauffmann and Grombach, *Ann.*, 344, **30** (1906).

[8] Auwers and Rietz, *Ber.*, 40, 3514 (1907).

It is suggested that the quinoid structure (B) represents the blood-red form, whose reduction should lead to (C) and (D), hydrolysis of which by the alkali should yield benzaldehyde.

The Pechmann Dye yields benzoic acid when oxidized by hot chromic acid mixture or alkaline permanganate; the dibenzoyl quinone described herein gives the same acid when oxidized cold by these reagents.

In glacial acetic acid solution both benzoyl quinones reacted instantly with aniline to form beautifully crystalline precipitates. That from the monobenzoyl derivative was deep purplish red and proved to be the dianilino-monobenzoylquinone. That from the dibenzoyl quinone was a monoanilino-dibenzoylhydroquinone and was bright yellow. Under similar conditions the Pechmann Dye condenses immediately with two moles of aniline to a dark green crystalline product which Kozniewski and Marchlewski[4] believed to be the dianilide of dibenzoyl quinone, but which the recent work of Bogert and Greenberg[9] has shown to be most probably the N,N′-diphenyl dilactam of diphenacylfumaric acid. In the case of both quinones the aniline appeared to act preferably upon the hydrogens of the nucleus, to form aniline derivatives, the dibenzoyl derivative, presumably because of its greater affinity for hydrogen, being reduced to the hydroquinone, whereas the monobenzoyl compound remained as the quinone; or, there may have occurred addition in both instances, followed by oxidation in the case of the monobenzoyl product and reduction in that of the dibenzoyl.

The latter hypothesis appears the more plausible in the light of the behavior of the two quinones with acetic anhydride containing a trace of concentrated sulfuric acid, following the method used by Thiele[10] for studying 1,4-addition to unsaturated γ-diketone types. Both quinones yielded the corresponding mono- and di-benzoylhydroxyhydroquinone triacetates, from which the hydroxyhydroquinones themselves were easily secured. So far as we are aware, this is the only method as yet described for the preparation of these diacylated trihydric phenols.

Inasmuch as in the formation of the Pechmann Dye from acetic anhydride and benzoylacrylic acid considerable amounts of unidentified by-products are separated, it seemed possible, were this dye actually a dibenzoylquinone, that some of these by-products might have been formed by addition reactions similar to the above, but a careful examination of them showed that they were not.

Experimental

1,4-Dimethoxybenzene.—The method used by Ullmann[11] for the preparation of this compound was modified as follows. To a solution of 50 g. of hydroquinone in 275

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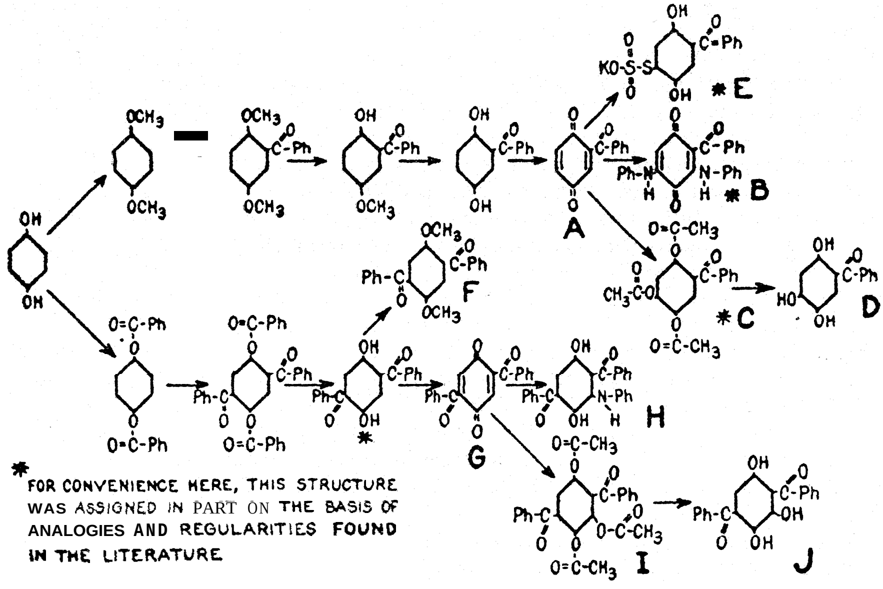
[9] Bogert and Greenberg, unpublished results. See "Dissertation" by Irving W. Greenberg, Columbia University, 1926.

[10] Thiele, Ber., 31, 1247 (1898).

[11] Ullmann, *Ann.*, **327,** 104 (1903).

cc. of 15% sodium hydroxide there was added slowly and with vigorous shaking 105 cc. of methyl sulfate, allowing the temperature to rise gradually to 50° until most of the methyl sulfate had been added, then interrupting its addition for a short time while continuing the shaking, finally running in the remainder and renewing the agitation for a further ten minutes. Excess of methyl sulfate was destroyed by addition of 50 cc. of 10% sodium hydroxide and heating for an hour at 100°. As the solution cooled, the dimethyl ether crystallized. It was collected, washed, dried and crystallized from 75% alcohol, when it appeared in large colorless lustrous flakes, of strong but agreeable ethereal odor, m. p. 56.8° (corr.); yield, 55.5 g., or 88.5%. Ullmann reported the m. p. as 56°.



*FOR CONVENIENCE HERE, THIS STRUCTURE WAS ASSIGNED IN PART ON THE BASIS OF ANALOGIES AND REGULARITIES FOUND IN THE LITERATURE.

Flow sheet.

Monobenzoylhydroquinone dimethyl ether (2,5-dimethoxybenzophenone), C_6H_5-$COC_6H_3(OCH_3)_2$, was prepared from hydroquinone dimethyl ether, benzoyl chloride and anhydrous aluminum chloride, in carbon disulfide solution, according to the process of Kauffmann and Grombach.[7] The crude product was freed from unaltered initial material and from the monomethyl ether (formed as a by-product to the extent of about 10%) by long continued and repeated steam distillation of a strongly alkaline solution. Crystallized from methyl alcohol, the benzoylated dimethyl ether was obtained in colorless crystals, m. p. 51.2° (corr.); yield, about 40%. Kauffman and Grombach reported a melting point of 51° for yellow crystals, Herzig and Hofmann[12] a melting point of 50–52° for colorless ones.

When this dimethyl ether was heated with constant-boiling hydrobromic acid for two and one-half hours at 130–140° in sealed tubes, hydrolysis apparently occurred, for the only product identified was benzoic acid.

Monobenzoylhydroquinone Monomethyl Ether (2-Hydroxy-5-methoxybenzophenone) $C_6H_5COC_6H_3(OH)OCH_3$.—By the following variations in the procedure employed for the synthesis of the dimethyl ether, the monomethyl ether was made the principal instead of the by-product. To a solution of 50 g. of hydroquinone dimethyl

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[12] Herzig and Hofmann, *Ber.*, 41, **143** (1908).

ether and 50 g. of benzoyl chloride in 50 cc. of carbon disulfide, there was added slowly (one and one-half hrs.) 60 g. of finely pulverized anhydrous aluminum chloride, the temperature of the mixture being kept at about 25°. After standing for forty-eight hours at room temperature, the reaction was completed by warming for thirty minutes at about 50°. The dark resinous mass was hydrolyzed with cracked ice and concentrated hydrochloric acid and the yellow product distilled with steam for two hours to free it from carbon disulfide and most of the unaltered initial hydroquinone dimethyl ether. The brown oil remaining was dissolved in ether, the ethereal solution dried with calcium chloride, the solvent evaporated, the brown oily residue dissolved in 75 cc. of dry benzene, and to this solution 35 g. of finely pulverized anhydrous aluminum chloride was added at such a rate as to maintain a brisk evolution of hydrogen chloride. After all of the aluminum chloride had been added, the temperature of the mixture was raised gradually to the boiling point and gentle refluxing continued until hydrogen chloride was no longer evolved. A deep red solution resulted which was cooled and decomposed by 6 N hydrochloric acid. Steam distillation removed the benzene and toluene (formed in the reaction), leaving a brown oil which changed to a yellowish solid as it cooled. This crude product was washed with water, dried, dissolved in a large volume of 70–75% alcohol and the solution allowed to cool slowly to room temperature.

A very impure product separated as a heavy dark oil and 30 g. of fairly pure material was recovered by chilling the decanted supernatant liquid. The impure heavy dark oily portion was dissolved in 10% sodium hydroxide with some difficulty, the alkali solution washed with ether and then acidified to faint turbidity. Precipitation was completed by saturating the solution with carbon dioxide. The precipitate was removed, washed with water and crystallized from 80% alcohol, giving 20.5 g. of bright yellow plates, m. p. 84–85.5° (corr.); total yield, 50.5 g., or 55%. Kauffmann and Grombach[7] gave the melting point as 78°, Herzig and Hofmann[12] as 82–85". Both groups of investigators obtained their product by the action of hydriodic acid upon the dimethyl ether.

A solution of 0.1 mole of monobenzoylhydroquinone dimethyl ether in 10 cc. of carbon disulfide was treated with an equimolar quantity of benzoyl chloride and anhydrous aluminum chloride, the mixture allowed to stand for twenty-four hours, then heated for three hours at 50–60° and worked up in the customary manner; the main product isolated was this same monomethyl ether (m. p. 84–85.5°, corr.), and no dibenzoyl derivative was obtained.

When this monomethyl ether was heated at 135–140" in sealed tubes with constant-boiling hydrobromic acid, hydrolysis apparently ensued, for the amount of benzoic acid isolated nearly equaled that calculated.

Monobenzoylhydroquinone (2,5-Dihydroxybenzophenone), C_6H_5CO-$C_6H_3(OH)_2$.—Klinger[13] has reported the formation of this compound when hydroquinone was heated with an excess of benzoic acid in the presence of anhydrous zinc chloride, following the analogous work of Nencki and Schmid,[14] whose experiments were conducted with aliphatic and not aromatic acids. Klinger stated further that his results with benzoic were much less favorable than with aliphatic acids, and that the principal product isolated was hydroquinone dibenzoate. Our experience with this process was less satisfactory even than Klinger's, for we succeeded in isolating only a trace of monobenzoylhydroquinone, the main product being, as he found, the hydroquinone dibenzoate (mixed m. p., 204°, corr.).

[13] Winger, *Ann.*, 382, 211 (1911).

[14] Nencki and Schmid, J. prakt. *Chem.*, [2] 23, 546 (1881).

The observation of Klinger and Standke[15] that monobenzoylhydroquinone was formed when a mixture of benzoquinone and benzaldehyde was exposed to the action of direct sunlight for long periods of time could not be utilized as the basis of a practical method of preparation.

Finzi[16] heated hydroquinone, or its dibenzoate, in nitrobenzene solution, with benzoyl chloride in the presence of anhydrous aluminum chloride and reported the formation of the keto derivative. Our repetition of this work, involving also several attempted variations, yielded, aside from the dihenzoate (mixed m. p., 204°, corr.), only dark colored decomposition products. These results are in agreement with those of Perrier,[17] who found that whereas aliphatic acid chlorides, in the presence of aluminum chloride, condensed with mononuclear phenols, in carbon disulfide solution, to keto derivatives, aromatic acid chlorides under the same conditions formed only the phenolic esters.

The Hoesch[18] reaction proved equally unsuccessful. This involved the action of dry hydrogen chloride upon a solution of hydroquinone and benzonitrile in dry ether, in the prrsence of anhydrous zinc chloride. No keto derivative was obtained. The sole product isolated, even when a large excess of the nitrile was present, was hydroquinone monobenzoate (colorless feathery needles; mixed m. p. 164.5' corr.).

Kauffmann and Grombach[7] were unsuccessful in their attempt to demethylate completely the benzoylhydroquinone dimethyl ether by refluxing it with three parts of constant-boiling hydriodic acid, for only one methyl group was removed. Two years later, Herzig and Hofmann[12] accomplished this demethylation by using six parts of hydriodic acid and long continued refluxing. Our own experience with this latter method was decidedly disappointing, both from the standpoint of time consumed (twelve hours) and yields *(5%)* of pure product.

We found, however, that benzoylhydroquinone monomethyl ether could be satisfactorily demethylated by the following process.

Sixteen parts of the monomethyl ether was refluxed for one and one-half hours with **2.5** parts of constant-boiling hydriodic acid, **20** cc. of glacial acetic acid and 4 cc. of acetic anhydride, and the clear orange solution poured into **100** cc. of cold water. The yellow crystalline precipitate was washed with water, dried and crystallized from benzene, when it formed yellow crystals, m. p. 125–126.1° (corr.); yield, **13 g.**, or **87%.** Herzig and Hofmann gave the melting point as 122–124°; Klinger and Standke[15] as 125".

Based upon an earlier observation of Weishut,[19] Pregl[20] recommended the addition of a few drops of acetic anhydride or a few crystals of phenol to the hydriodic acid mix-

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[15] Klinger and Standke, *Ber.*, **24, 1340 (1891).**

[16] Finzi, *Monatsh.*, **26, 1119 (1905).**

[17] Perrier, *Compt. rend.*, 116, **1140 (1893).**

[18] Hoesch, *Ber.*, **48, 1122 (1915).**

[19] Weishut, *Monatsh.*, 34, 1549 **(1913).**

[20] Pregl, "Quantitative Organic Microanalysis," translated by Fyleman, Philadelphia, P. Blakiston's Son and Co., **1924**, p. 153.

ture when determining quantitatively the methoxyl group in ethers which are difficult to demethylate. The accelerating influence of these additions upon the rate of demethylation has been ascribed to increased solubility effect. In the demethylation of the monomethyl ether as carried out by us, glacial acetic acid was an excellent solvent and worked well alone, but the addition of the acetic anhydride appeared to bring the reaction to completion in less time.

Monobenzoyl-*p*-benzoquinone, $C_6H_5COC_6H_3O_2$.—A solution of 10 g. of monobenzoylhydroquinone in 50 cc. of glacial acetic acid was added very slowly (twenty minutes) to a mixture of 8 g. of sodium dichromate, 10 cc. of concentrated sulfuric acid and 350 cc. of water, while the temperature was maintained in the vicinity of 10° and the solution was vigorously stirred. This stirring was continued for about ten minutes after all of the hydroquinone had been added and until the color of the mixture changed to a dark reddish brown. The suspended product was immediately filtered out, washed well with water and dried. It amounted to about 9 g. Recrystallized from 500 cc. of ligroin (b. p. 70–100), it gave 7.5 g. of orange yellow lustrous flattened needles, m. p. 85–85.6° (corr.); yield, 77%. The chief impurity in the crude product seemed to be a trace of benzoic acid.

The recrystallization from ligroin proved quite troublesome, because of the tendency of the solution to separate a dark brown difficultly soluble precipitate. This was avoided by adding the finely powdered crude product to the boiling solvent with simultaneous mechanical stirring.

Anal. Calcd. for $C_{13}H_8O_3$: C, 73.57; H, 3.81. Found: C, 73.47; H, 3.83.

The purified quinone was soluble in most of the usual neutral organic solvents. In hot water it dissolved but slightly, giving a reddish solution, due perhaps to some incipient chemical change. It was attacked by dilute aqueous caustic alkali, with formation of a brownish solution, from which a light brown flocculent precipitate containing some benzoic acid was thrown down on acidification. It was easily reduced by sulfurous acid to the original hydroquinone again. With hydroxylamine, under various conditions, the quinone failed to yield sufficient oxime to be isolated and identified, probably due to the sensitiveness of the quinone to the reducing action of the hydroxylamine.

Dianilino-monobenzoyl-*p*-benzoquinone, $C_6H_5CO(C_6H_5NH)_2C_6HO_2$.—A solution of 2 g. of aniline in 4 cc. of glacial acetic acid was added to one of 1.6 g. of monobenzoyl quinone in 20 g. of the same solvent while warm. The mixture turned deep red immediately. After warming for a few minutes longer, it was left for half an hour at room temperature and was then stirred vigorously. A deep purplish red crystalline precipitate separated and the separation was complete at the end of an hour. The precipitate was collected, washed with glacial acetic acid, then with alcohol, dried and recrystallized from a large volume of alcohol. As thus purified, the product formed diamond-shaped plates which appeared red by transmitted and purple by reflected, light, m. p. 211.7–212.2" (corr.). From a small volume of hot benzene clusters of small purplish red plates were obtained, m. p. 212.2–212.7" (corr.); yield, about 1 g., or 34%.

Anal. Calcd. for $C_{25}H_{18}O_3N_2$: C, 76.09; H, 4.60. Found: C, 76.17; H, 4.62.

This method of preparation resembles that used by Zincke and Hagen[21] for the preparation of anilino derivatives of p-benzoquinone itself, except that with this acyl derivative the formation of dianilino-anilide was not observed.

This dianilino-benzoyl-quinone was unaffected by hot sulfurous acid, and was not acetylated when heated with acetic anhydride and fused sodium acetate, a behavior which has been observed before[22] in the case of such dianilino derivatives. In con-

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[21] Zincke and Hagen, *Ber.*, 18, 785 (1885).

[22] Fischer and Hepp, *ibid.*, 21,683 (1888).

centrated sulfuric acid it dissolved slowly to a deep red solution, but was insoluble in dilute acid or in alkali.

Monobenzoylhydroxyhydroquinone Triacetate, $C_6H_5COC_6H_2(OCOCH_3)_3$.—The Thiele[10] method for effecting 1,4-addition to unsaturated γ-diketones was applied to the benzoyl quinone with interesting results.

To 6 g. of acetic anhydride, containing three drops of concentrated sulfuric acid, there was added 2 g. of the benzoyl quinone and the reaction was completed by warming for two to three minutes at 40-50°. The yellow solution gradually lost nearly all of its color. It was poured into cold water and the mixture allowed to stand until the hydrolysis of the excess of acetic anhydride was completed. The colorless precipitate was removed, washed with water, dried and crystallized from alcohol, when it appeared in glistening colorless needles, m. p. 137.7° (corr.); yield, 1.1 g.

Anal. Calcd. for $C_{19}H_{16}O_7$: C, 64.03; H, 4.53. Found: C, 63.86; H. 4.53.

In cold 0.5 N caustic alkali the compound was insoluble, but when heated it gave a greenish black solution apparently due to hydrolysis and subsequent oxidation. Attempts to convert this triacetate, by the action of methyl sulfate and alkali, into the 2,4,5-trimethoxybenzophenone of Bargellini and Martegiani[23] were unsuccessful.

Monobenzoylhydroxyhydroquinone, $C_6H_5COC_6H_2(OH)_3$.—A solution of 2 g. of the above triacetate in 20 cc. of absolute alcohol saturated with dry hydrogen chloride was refluxed for about two hours, the alcohol and ethyl acetate then removed by distillation under diminished pressure and the residual reddish oil shaken with cold water. The yellow crystalline mass thus formed was filtered out, washed with water, dried and crystallized from a mixture of equal parts of benzene and ligroin (b. p. 70–100°). Fine orange yellow crystals were thus obtained, m. p. 129.1" (corr.); yield, 1 g., or 77%.

Anal. Calcd. for $C_{13}H_{10}O_4$: C, 67.84; H, 4.38. Found: C, 68.00; H, 4.45.

The compound dissolved in dilute aqueous caustic alkali to a reddish orange solution which changed to a greenish black after a brief exposure to the air. Acidification of the reddish orange solution re-precipitated the original benzoylhydroxyhydroquinone, but this did not occur in the case of the greenish black solution. This hydroquinone stained the skin a rather fast black.

Monobenzoylhydroquinone Thiosulfuric Acid, $C_6H_5COC_6H_2(OH)_2SSO_3H$.—Patents were taken out in 1908 by the Badische Anilin und Soda-Fabrik[24] for the production of hydroquinone thiosulfuric acids from *p*-quinones and for their utilization as dye intermediates. Hydroquinone thiosulfuric acid is described therein as being easily condensed with 2-amino-5-dimethylaniline thiosulfuric acid in alkaline solution by means of air oxidation to give a blue violet dye. The specifications of these patents were applied, with minor changes, to the monobenzoyl quinone as follows.

A warm (40–50°) solution of 5 g. of monobenzoylquinone in 28 cc. of glacial acetic acid was run into a solution of 9 g. of sodium thiosulfate in an equal weight of water, while the temperature was maintained within a few degrees of that of the room. After standing for two hours at room temperature, the clear yellow solution had deposited a small amount of benzoylhydroquinone as a fine yellow solid and more was separated by addition of several volumes of water. The mixture was allowed to stand for an hour more, the suspended benzoylhydroquinone filtered out and the filtrate saturated with potassium chloride. The potassium salt of the thiosulfuric acid separated in pale yellow crystals, which were collected, washed with a 5% potassium chloride solution, then with water and finally with alcohol. The dried product (6 g.) was recrystallized from hot

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[23] Bargellini and Martegiani, *Gazz. chim. ital.*, *41*, II, 603 (1911).

[24] (a) German Patent 175,070, *Friedländer*, 8, 140 (1908); (b) German Patent 178,940, *Friedlander*, 8, 756 (1908).

water by salting out with potassium chloride and washing as before. As thus purified it formed pale yellow lustrous crystalline flakes which decomposed near 240° without previous melting; yield, 5.1 g., or 60%.

In its analysis the potassium was determined by an adaptation of the process of Pregl,[25] and the sulfur by the Carius method.

Anal. Calcd. for $C_{13}H_9O_6S_2K$: C, 42.83; H, 2.49; K, 10.73; S, 17.51. Found: C, 43.21; H, 2.40; K, 10.49; S, 17.53.

This salt was insoluble or difficultly soluble in most of the commoner neutral organic solvents, but could be crystallized from a large volume of alcohol. Its solubility in cold water was low, but rose rapidly with rise in temperature. Concentrated sulfuric acid turned the crystals red and then slowly dissolved them to an orange solution. The salt appeared to be stable in 2 N sulfuric acid. In 0.5 N caustic alkali it dissolved to an orange solution.

This thiosulfate was treated with an equal weight of 2-amino-5-diiethylaniline thiosulfuric acid in a 20% sodium carbonate solution and oxidized by the air, following the process of the patent and the method used by Heller, Quast and Blanc[26] for the synthesis of Brilliant Alizarine Blue. These latter authors found that the thiosulfuric acid of hydroquinone gave more than one product when carried through this condensation, and our experience with the thiosulfuric acid described above was similar, the product consisting chiefly of deep reddish violet crystals mixed with a bluish black amorphous solid. The reddish violet crystals dissolved in glacial acetic acid, acetone or nitrobenzene to a bluish solution, and in benzene to a reddish violet one. The fact that a violet dye, presumably a thiazine, was formed in this condensation argues in favor of the assumption that in the original benzoylhydroquinonethiosulfuric acid the benzoyl was not adjacent to the thiosulfuric group.

Hydroquinone dibenzoate, $C_6H_4(OCOC_6H_5)_2$, was prepared from hydroquinone and benzoyl chloride, as described by Doebner and Wolff,[6] who gave the melting point as 199°. Our product crystallized from toluene in large flat needles, which were washed with hot alcohol and dried, and then melted at 204° (corr.); yield, 90%.

Dibenzoylhydroquinone $(C_6H_5CO)_2C_6H_2(OH)_2$.—Doebner and Wolff[6] reported the synthesis of this compound from hydroquinone dibenzoate and two moles of benzoyl chloride in the presence of small amounts of anhydrous aluminum chloride, at 190–200°, followed by hydrolysis of the product. All attempts to repeat this work, following carefully the rather vague and sketchy outline of the process as given by these investigators, resulted in excessive charring and a yield of pure product amounting to about 2%.

Böeseken[27] has reported that benzoyl chloride was decomposed by anhydrous aluminum chloride above 170° but, on studying this matter further, it was learned that considerable decomposition occurred at temperatures as low as 160°. The cause of the extensive charring in this dibenzoylhydroquinone synthesis was probably due, at least in part, to this decomposition of the benzoyl chloride, yet when the reaction was conducted at 165–175°, or at 175–185°, the charring increased and only a trace of the diketo derivative was obtained, whereas if the temperature was maintained at 200–205° and the aluminum chloride was added in small portions and at sufficiently wide intervals of time as to insure a slow and steady evolution of hydrogen chloride, the yield of the compound sought was raised to 12–15% of that calculated.

In this way a solution of 50 g. of hydroquinone dibenzoate in 49 g. of benzoyl chloride, kept at 200–205°, was treated with about 10 g. of aluminum chloride, in 0.5-g.

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[25] Pregl, Ref. 20, p. 135.

[26] Heller, Quast and Blanc, *J. prakt. Chem.*, [2] 108, 257 (1924).

[27] Böeseken, *Rec. trav. chim.*, 27, 10 (1908).

portions, until at the end of forty-eight hours the reaction was complete. The black tarry product when cold was treated with 300 cc. of 15% alcoholic potassium hydroxide, the mixture boiled for two hours, the alcohol distilled off, the residue treated with water, filtered and the blood red filtrate saturated with carbon dioxide. The diketo compound precipitated mixed with brownish impurities (mainly aluminum compounds). It was collected, washed with water and with 1 *N* hydrochloric acid, dried (weight, 8 g.) and recrystallized from alcohol in the presence of norite until the melting point remained constant at 210.5–211.1° (con.). It formed fine yellow needles; yield, 12–15%. Doebner[28] gave the melting point as 206°, when crystallized from alcohol, and 207" from toluene.

The substitution of anhydrous ferric chloride for part or all of the aluminum chloride in this synthesis, or the use of nitrobenzene as solvent, seemed to do more harm than good.

Following the experiments of Klinger and Standke[15] for the production of monobenzoylhydroquinone from benzoquinone, a small quantity of monobenzoyl-*p*-benzoquinone was dissolved in excess of benzaldehyde and the solution exposed to direct sunlight. After standing for many days the solution became quite dark, but no crystalline material separated, and the experiments were discontinued.

Although it seemed highly probable that in this dibenzoyl derivative the two benzoyl groups were in the para relation to each other, because of the strong ortho-orienting influence of the hydroxyl groups, some experiments were carried out in the hope of obtaining practical proof of the truth of this assumption.

Efforts to reduce the two benzoyl groups to hydrols by the use of sodium amalgam, in either alkaline, alcoholic or glacial acetic acid solution, failed to give the desired product, although Doebner[B] successfully reduced p-benzoylphenol to the benzohydrylphenol in this way.

Doebner also obtained *p*-hydroxybenzoic acid from p-benzoylphenol by fusion with caustic alkali, but dibenzoylhydroquinone was instantly decomposed by such treatment.

Attempts to obtain bromine derivatives likewise proved fruitless, irrespective of variations in solvent, temperature or other factors.

Dibenzoylhydroquinone Dimethyl Ether, $(C_6H_5CO)_2C_6H_2(OCH_3)_2$.—To a solution of 2 g. of dibenzoylhydroquinone in 40 cc. of 20% sodium hydroxide, 10 cc. of methyl sulfate was added slowly while the solution was stirred vigorously, and well cooled until the end of this addition, when it was permitted to rise to about 50°. The original blood red color of the solution changed to yellow and a pale yellowish precipitate separated. Excess of methyl sulfate was destroyed by addition of more alkali and heating at 100°. The precipitate was collected and crystallized from either alcohol or glacial acetic acid, when it appeared in colorless dendritic flakes, m. p. 124–124.5°; yield, nearly that calculated.

Anal. Calcd. for $C_{22}H_{18}O_4$: C, 76.26; H, 5.24. Found: C, 75.61; H. 5.08.

It was insoluble in cold or in hot 10% sodium hydroxide. Heated for half an hour with two parts of constant-boiling hydriodic and one of glacial acetic acid, it was smoothly demethylated to the original dibenzoylhydroquinone.

An attempt to prepare this dimethyl ether by further benzoylation of the monobenzoyl dimethyl ether resulted in the elimination of the methyl from the methoxyl in Position 2, as already noted, and no dibenzoyl derivative was obtained.

Dibenzoyl-*p*-benzoquinone, $(C_6H_5CO)_2C_6H_2O_2$.—A solution of 4 g. of dibenzoylhydroquinone in 75 cc. of warm glacial acetic acid was oxidized by a mixture of 10 g. of sodium dichromate, 10 cc. of concentrated sulfuric acid and 250 cc. of water, in

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[28] Doebner, Ann., 210, 246 (1881).

essentially the same way as already described for the oxidation of the monobenzoylhydroquinone. The crude product was crystallized from a large volume of ligroin (b. p. 100–108°) and was thus obtained in orange needles, m. p. 164–164.5° (corr.); yield, 2.3 g., or 60%. This crystallization encountered the same obstacles that were noted for the monobenzoyl derivative and hence had to be carried out with similar precautions.

Anal. Calcd. for $C_{20}H_{12}O_4$: C, 75.93; H, 3.83. Found: C, 75.80; H, 3.94.

It was more or less soluble in most of the common neutral organic solvents and was moderately soluble in hot water with formation of a reddish orange solution. Toward caustic alkali it was much more stable than the monobenzoyl quinone. It was easily oxidized by cold alkaline permanganate and more slowly by chromic acid mixture. In both cases the product was benzoic acid. By sulfurous acid it was readily reduced to the original hydroquinone. With hydroxylamine its behavior was much the same as that of the monobenzoyl quinone, indicating that it too probably functioned as an oxidizing agent.

Monoanilino-dibenzoylhydroquinone, $(C_6H_5CO)_2(C_6H_5NH)C_6H(OH)_2$.—When a solution of 0.45 g. of dibenzoyl quinone in warm glacial acetic acid was treated with 0.4 g. of aniline in the same solvent, fine glistening scales soon separated from the dark solution and this separation was complete after thirty minutes' standing. The greenish yellow crystals were removed, washed with glacial acetic acid, then with alcohol, dried and recrystallized from alcohol, when they appeared as fine lustrous yellow plates, which became orange at about 225°, decomposed slightly at about 228°, and melted at 234.9–236.8° (corr.); yield, 0.3 g., or 52%.

Anal. Calcd. for $C_{26}H_{19}O_4N$: C, 76.25; H, 4.68. Found: C, 76.33; H, 4.66.

The compound dissolved slowly in cold dilute caustic alkali, but quickly in the hot to a deep orange solution which changed to yellow as it cooled.

Although we varied the conditions under which the quinone and aniline were brought together, we failed to isolate any product corresponding to that obtained from the Pechmann Dye and aniline and which Kozniewski and Marchlewski[4] believed to be a dibenzoylquinone dianilide, $(C_6H_5CO)_2C_6H_2({=}NC_6H_5)_2$.

Dibenzoylhydroxyhydroquinone triacetate, $(C_6H_5CO)_2C_6H(OCOCH_3)_3$, was prepared from the dibenzoyl quinone (1 g.), acetic anhydride (3 g.) and a few drops of concentrated sulfuric acid, as described for the monobenzoyl compound. After standing for a few minutes at 40–50°, the orange color of the solution faded to pale yellow. It was poured upon cracked ice and left long enough to hydrolyze the excess of acetic anhydride without decomposing the readily hydrolyzable triacetate. The pale yellow oily product finally congealed to a nearly colorless solid, which was removed, washed with water, then with 50% alcohol, dried and crystallized from alcohol. It formed colorless glistening flakes, m. p. 120–120.5° (corr.); yield, 0 9 g., or 62%.

Anal. Calcd. for $C_{26}H_{20}O_8$: C, 67.79; H, 4.38. Found: C, 67.85; H, 4.44.

The product was insoluble in cold dilute caustic alkali, but dissolved in it when hot, with simultaneous hydrolysis and formation of an orange solution.

Dibenzoylhydroxyhydroquinone, $(C_6H_5CO)_2C_6H(OH)_3$.—A solution of 0.5 g. of the above triacetate in 5 cc. of alcohol containing 0.5 cc. of concentrated hydrochloric acid was heated for an hour at 100° and the resultant deep yellow solution diluted with an equal volume of water. As the solution cooled fine needles of the hydroxyhydroquinone separated in nearly theoretical yield. Recrystallized from 50–60% alcohol, rosets of yellow needles were obtained, m. p. 196.9–197.5"; yield, 0.3 g., or 83%.

Anal. Calcd. for $C_{20}H_{14}O_5$: C, 71.83; H, 4.22. Found: C, 71.47; H, 4.21.

This trihydric phenol dissolved in dilute caustic alkali to an orange solution, which was quite stable toward air oxidation, for after standing for several minutes in the air acidification precipitated the unaltered original phenol.

Comparative Oxidation and Reduction Reactions of the Benzoylhydroquinones and Benzoylquinones

Acid Oxidation of the Benzoylhydroquinones.—Oxidation of the two hydroquinones with the same dilute chromic acid mixture, under identical conditions, showed that the dibenzoyl derivative was much more difficult to oxidize and considerable of the original hydroquinone was recovered unchanged.

Alkaline Oxidation of the Benzoylhydroquinones.—When dilute blood red alkaline solutions of equimolar concentrations of the two hydroquinones were exposed to the air for a short time and then acidified with dilute mineral acid, the original yellow hydroquinones were precipitated unaltered. On longer exposure of these solutions, however, that containing the monobenzoyl derivative turned dark brown before the color of the other underwent any change at all, and acidification of the two solutions precipitated only the dibenzoyl derivative unaltered. When these same original alkaline solutions were protected from the air, both were quite stable for the periods of time used in the experiments just mentioned.

Similar results were noted when hydrogen peroxide was used, in place of air, as the oxidizing agent. Dark brown solutions were obtained in both cases, but the original blood red color of the alkaline monobenzoyl solution changed much sooner than that of the dibenzoyl derivative. From both of these brown solutions, acidification precipitated a pale brown solid, from which benzoic acid was the only product isolated. The corresponding quinones may have been formed as intermediate products in this oxidation, but they were not detected and may have been changed as rapidly as formed to benzoic acid by the alkaline oxidizing medium.

Reduction of Mono and Dibenzoylquinones.—Equimolar concentrations of the two quinones in glacial acetic acid were treated with saturated sulfurous acid under identical conditions. Both quinones were thus reduced to their hydroquinones, but the reduction was more rapid and more nearly complete (for the same time interval) with the dibenzoyl than with the monobenzoyl derivative. This is in harmony with the oxidation experiments recorded above and indicates that the dibenzoylquinone has the greater affinity for hydrogen and hence probably the higher reduction potential.

Tinctorial Properties of the Mono- and Dibenzoylquinones.—Some unbleached wool was heated for thirty minutes at 100° in a 3% solution of monobenzoyl quinone in glacial acetic acid. The wool was dyed a dark reddish shade, while the dye bath retained its original yellowish orange color. Washed thoroughly with warm glacial acetic acid, then hot water and dried, the dyed wool appeared reddish-brown. This dyeing was quite fast to washing and to acid, but not to light, stoving, bleaching or alkali.

Similar experiments carried out with the dibenzoyl quinone gave similar results, except that the shade produced was more reddish and less intense and the dyeings rather less fast.

Because of the depth and richness of the color of the dianilino derivative of the monobenzoylquinone and its great stability toward acids, alkalies and other reagents, attempts were made to obtain fast dyeings by precipitating this compound within the fibers of the cloth. Unbleached wool was treated therefore with a 5% solution of the monobenzoyl quinone in glacial acetic acid and a solution of aniline in the same solvent was then added to this impregnated wool. The fabric was dyed a reddish shade, but much paler than the dye bath even after warming for an hour at 100°. In other experiments conditions were varied but the dyeings remained unsatisfactory in depth and quality.

Summary

1. Benzoylated *p*-benzoquinones have been synthesized and studied, with results which support the constitutional formulas determined by Bogert and Ritter for the "Pechmann Dyes," rather than those proposed by Kozniewski and Marchlewski.

2. The acylated quinones represent a group hitherto unknown; their properties are therefore of interest.

3. Methods have been developed for the production of benzoylhydroquinones, which compounds are oxidized readily to the corresponding quinones.

4. The behavior of the benzoylquinones with aniline and with acetic anhydride has been studied and benzoyl hydroxyhydroquinones have been obtained.

5. Tests of the comparative stability of mono- and dibenzoyl quinones to oxidizing and reducing agents have been conducted, and some interesting problems concerning the structure of the benzoylhydroquinones are pointed out.

6. The synthesis and properties of other new compounds are described.

NEW YORK, N. Y.

NEW BOOKS

General Chemistry. A Text-book for College Students. By JOSEPH A. BABOR, Assistant Professor of Chemistry, College of the City of New York. Thomas Y. Crowell Company, 393 Fourth Avenue, New York, 1929. x + 586 pp. 167 figs. 14.5 X 22.5 cm. Price, $3.75.

This book has been written for the use of college students who have had a preparatory course in chemistry. With this background in mind the author has left out some of the descriptive material usually found in elementary text-books of chemistry. The distinctive feature of the text is the extensive application of the principles of atomic structure, which is introduced early in the course. In the preface the author states that "Not only is the concept introduced, but constant use is made of it throughout the course, for atomic structures furnish the tools with which to study the chemical properties of the elements. Before the properties of an element are discussed the atomic structure of that element is studied and compared with the atomic structures of other elements in the same family, and the chemical properties of the element in question are predicted." The author accordingly uses a large number of diagrams to illustrate atomic structures and all oxidation–reduction equations are treated from the point of view of the electronic changes. This has been well done and will make a strong appeal to many teachers of chemistry.

The discussions of some of the topics considered by many as essential parts of a course in general chemistry are omitted altogether or treated very briefly. While some of this material may have been included in the secondary school course in chemistry that is required for the user of this book, this is not always the case, at least in the average high school. For example, in view of the general and increasing importance of dispersed systems, it seems a pity to limit the discussion of this subject to less than one page.

Considerable space is given to a rather detailed and well presented discussion of the dissociation theory but no mention is made of the important modifications in this theory which have resulted from the work of Bragg and of Debye and Hückel.

The following statement on page 113 will be questioned by many: "We have learned that molecular oxygen is inactive but that atomic oxygen acts readily. It is possible that the water vapor causes dissociation of some molecules of oxygen into atoms, or produces a weakening of the non-polar bonds of the molecule. Such atoms or weakened molecules react. The same explanation is offered for the activity of chlorine."

The book is well printed and attractively bound, the proof reading has been carefully done, and the illustrations are excellent.

JAMES H. WALTON

Laboratory Manual in General College Chemistry. By JOSEPH A. BABOR, Assistant Professor of Chemistry, College of the City of New York, and ALEXANDER LEHRMAN, Instructor in Chemistry, College of the City of New York. Thomas Y. Crowell Company, 393 Fourth Avenue, New York, 1929. viii + 376 pp. 34 figs. 14.5 X 22.5 cm. Price, $2.00.

This manual, which is written for use with Babor's General Chemistry, contains 142 experiments on some of the more fundamental theories and the commoner metals and non-metals and their more important compounds. The directions are clear and sufficiently detailed and each experiment is preceded by a discussion of the topic under consideration. The intelligent performance of these experiments should give the student a good comprehension of the fundamentals of elementary chemistry.

JAMES H. WALTON

Thermodynamik. (Thermodynamics.) By W. SCHOTTKY, H. ULICH and C. WAGNER. Julius Springer, Berlin, Germany, 1929. xxv + 619 pp. 90 figs. Price, paper cover, M. 56; bound, M. 58.8.

The three authors, one a theoretical physicist with strong engineering interests, the other two physical chemists, have written the most complete modern textbook on thermodynamics I know of. The subjects treated are the ones of most interest to the chemist, while purely engineering examples (internal combustion engine, e. g.) are scarcely mentioned.

The book uses chiefly the method of thermodynamic functions, which grows more and more common at present, but explains also the older methods. Furthermore, it has the great advantage of giving as standard values for energy and particularly entropy the ones referred to room temperature, as used in this country, as well as the ones referred to the absolute zero as used in Germany, so that the student can read papers of both kinds easily. In accord with G. N. Lewis' procedure, the authors introduce a number of newly defined quantities to make each step in the calculations clearer, by dividing the work necessary to perform a complicated process into standardized parts. While in the long run the result will probably be a clarification, it makes the book not easy to read.

In general, the characteristic features of the book are: a very thorough discussion of the fundamental assumptions; mainly considered in the first third of the book. The authors are not afraid to transgress occasionally beyond the limits set to thermodynamics by the purists. In this part they encounter the familiar difficulty of saying exactly what is meant by "molecule" in the condensed states. Instead of using this concept, they introduce the more general "resistant group" that might or might not coincide with it.

In the remaining two-thirds the authors proceed to the chemical applications. In this part are especially notable: the most thorough and detailed discussion of the chemical constant of ideal gases, and the influence of the "Statistical weight" upon it, which includes the latest results of the new quantum mechanics; a short presentation of the geometric methods, inaugurated by Gibbs and at present usually only found in books by Dutchmen, the scope of which is usually limited in other directions; detailed methods to be applied in reactions of non-ideal gases.

Finally, there is a treatment of equilibria with general solid phases which bridges a gap found in all other books. One is accustomed to give actual formulas for reactions in a gas and in solution, but if solids enter (apart from the simple case of pure solids, as in simple evaporation, dissolution and so on), one has to use the more qualitative statements of the phase rule and diagrams. This textbook is the first which tries to give actual formulas in these cases also. It thus starts a development which will, it may be hoped, make the equilibria with solids, which are of the highest technical importance (metallurgy!) as completely subject to calculation as the gases are now. The last sixty-four pages are devoted to numerical examples.

My main objection is that the prominence they merit is not given to the results of Stern's paper on the statistical foundations of the theory of solutions, which is far too little known, but which made the general theory clear for the first time.

If, finally, we compare this book with Lewis and Randall's well-known work, a comparison which arises naturally, I would say that Lewis and Randall could be compared to an automobile map, showing the highways in a clear and pleasant manner and leading the man who wants to get quickly to the big cities in an almost foolproof way. The present book is a mountain map, destined for the man who does not mind climbing over rather rough and desert country and spending much time over it and who enjoys it. Such a map is almost confusing in its details, but it shows how to get anywhere, including spots which are visited only very seldom.

KARL F. HERZFELD

A Concise Summary of Elementary Organic Chemistry. By FREDERICK HURN CONSTABLE, M.A., D.Sc. (London), F.T.C., Fellow of St. John's College, Camhridge. E. P. Dutton and Company, Inc., 286–302 Fourth Avenue, New York, 1929. xii + 149 pp. 13 X 19 cm. Price, $2.00.

The character of this book is indicated adequately by the title; it presents the essential facts of elementary organic chemistry in the form of an outline, and it is intended for the use of the student preparing for an examination. The book "tabulates series of compounds, giving their formulas; physical properties; the general methods of preparation; and the general reactions of the series. Finally, special examples of each series are described." It has been prepared carefully and the information given is well arranged and usually accurate. The only serious errors discovered consist in the writing of esterification as an irreversible reaction and in defining condensation, in connection with aldol formation, as an irreversible process.

If properly used, the new book should be an aid to the student in systematizing his information; but, since it emphasizes fact to the practical exclusion of theory, there is considerable danger that it will tend to lead the student to neglect the broader aspects of the subject. The student is expected to acquire from other sources a knowledge of general structural theory and the relationships between the different series; the limits of reactions, the reasons for the conditions required for bringing them about, and their application in syntheses. The present outline, however, hardly encourages this type of studying. The implication given is that, in preparing for an examination, an acquaintanceship with a large number of facts is more desirable than a thorough understanding of relatively few principles. The reviewer, on the other hand, has a partiality for the kind of examination which would be exceedingly difficult for the student whose knowledge of organic chemistry consisted solely in having memorized Dr. Constable's "Summary."

LOUIS F. FIESER

An Introduction to Modem Organic Chemistry. By L. A. COLES, B.Sc. (London), A.I.C., Senior Chemistry Master, Batley Grammar School. Longmans, Green and Co., 55 Fifth Avenue, New York, 1929. xv + ,452 pp. 78 figs. Illustrated. 13.5 × 20 cm. Price, $2.50.

This is a book for the student of high school or preparatory age who intends from the start to specialize in chemistry. Since in this country organic chemistry is seldom offered at this early stage in the student's training, the book can be evaluated only in terms of its suitability for use in our colleges. While it cannot be dismissed on the ground that it is too elementary for this purpose, it would be a difficult book to use in most institutions because of the unusual method of presentation adopted by the author.

The student's introduction to the new science is by way of the laboratory. He first prepares ethyl alcohol from sugar, without knowing anything about the structures of these compounds, and he then proceeds to prepare nearly all of the simple derivatives and oxidation products of the alcohol. He performs qualitative analyses and molecular-weight determinations with these compounds and learns how they may be analyzed quantitatively. After completing a similar experimental study of acetic acid, and a total of thirty-one experiments, he is at last given a chance to consider what it is all about. Then, with a few promptings from the author, he sees that he has already "discovered" the structures of the compounds with which he has been working. The second and third sections of the book present the essential facts about the aliphatic and aromatic compounds in more or less orthodox fashion, though the descriptive and theoretical matter is combined with laboratory experiments. The final chapter outlines the history of the science.

While the author is to be congratulated for the skill with which he has developed the idea of the purely experimental approach to learning, one questions the soundness of this policy. The advantage which may derive from familiarizing the student with a number of organic compounds before he commences the study of their structures is offset by the harm that may be done in teaching him to follow instructions which he cannot understand thoroughly. In launching the student into such a flood of laboratory work, the author also seems to be aiming at the ideal of having the student learn for himself. No one can quarrel with this excellent principle, but, unfortunately, it is not very practical. The student eventually has to be told almost everything, and it is only giving to the so-called experiment an illusory value to withhold some of the information available until after its completion.

The book is clearly written, the experiments are usually well planned, and the method of presentation is certainly novel. On the other hand, there are no special features which adequately justify the term "modern" in the title. This only tempts the reviewer to be over-critical and to point out that some of the apparatus described, as well as the systematic nomenclature, does not conform to the best current practice. **A** more serious charge is that no emphasis has been placed on the importance of unsaturation in organic chemistry. The double bond is first discussed on page 256, and there is very little mention of the activating influence of unsaturated groups in either the aliphatic or the aromatic series. The student will perhaps observe that the groups which are usually meta-directing, and which render benzene-substitution more difficult, are all unsaturated, but this is not called to his attention.

Lours F. FIESER

Les Essences Naturelles. Extraction—Caractbres—Emplois. (The Natural Essences. Extraction—Characteristics—Uses.) By PROFESSOR CALISTO CRAVERI, **translated from** the **second Italian Edition by** HENRI TATU. **Dunod, 92, Rue Bonaparte** (VI), **Paris, France, 1929. xi** + 602 **pp. 57 figs. 14 X 21.5 cm. Price, unbound, 70 fr.; bound, 80 fr.**

In the preface to this volume the author states his purpose to be the presentation of a manual of a practical nature, containing definite and precise information, exact figures, clear and conscientious advice and not to include material of a theoretical, hypothetical and polemical nature. The translator remarks that Mr. Craveri's work contains in a single volume the essentials of what is found in the largest works on the subject.

The book is divided into eight chapters, including general properties, physical and chemical characteristics of constituents, general methods of extraction, purification and preservation, general methods for the separation of constituents, concentration and deterpenation, general methods of analysis and classification of essences.

While the work intentionally subordinates the theoretical to the practical, too great condensation of chemical information is liable to lead to erroneous conclusions on the part of the reader, as, for example, the statement on page 48 that menthocitronellol is prepared artificially by the reduction of 1-menthone. As a matter of fact this transformation involves the preparation of at least four intermediates with a breaking of the ring structure.

This is an excellent manual on the subject of essential oils, and the impression gained from reading it is that the author has well accomplished his object as stated in the preface. A few typographical errors were noted, particularly in English and German synonyms, as in the misspelling of peppermint, tansy, myrtle and rainfarn.

E. K. NELSON

The Chemistry of Leather Manufacture. BY JOHN ARTHUR WILSON, D.Sc., Chief Chemist, A. F. Gallun and Sons Corporation; President, American Leather Chemists' Association. Volume II, second edition. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York, 1929. 685 pp. Illustrated. 15.5 × 23.5 cm. Price, $10.00.

The second volume of Dr. Wilson's outstanding contribution to the science and practice of leather making has been written with the same care and vigor as Volume I. The book is unique in its field for several reasons: it is the most comprehensive treatise on the subject; it covers the practical side in a simple expository manner, ignoring the many cook-book recipes once so popular in technological writings in the leather field; it gives a clear, concise and complete exposition of the latest known pure science foundations of the practical operations and materials, weaving the latter into the discussion of the manufacturing practice, and includes the fullest discussion now extant concerning the physical and chemical properties of different kinds of leather. The last named information has been created almost entirely through the author's own efforts.

The 29 chapters of the book include the following subjects: vegetable, chrome, alum, iron, oil, aldehyde, quinone, syntan and the rarer tanning processes; oil emulsions; fat liquoring; dyeing and finishing, including varnishes and lacquers; furs; microsectioning and microscopic technique; the physical and chemical properties of leather and methods of analysis. It is richly illustrated with photomicrographs, containing 59 plates on heavily sized paper and 159 figures.

This volume joins Volume I as an indispensable part of the library of leather chemists and tanners and will be found exceedingly useful to all chemists.

ARTHUR W. THOMAS

The Journal of the
American Chemical Society

VOL. 52 MARCH, 1930 No. 3

THIRTY-SIXTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED DURING 1929

BY GREGORY PAUL BAXTER

RECEIVED FEBRUARY 10, 1930 PUBLISHED MARCH 6, 1930

In the report of the German Committee on Atomic Weights for 1928,[1] the table of atomic weights is essentially identical with the American report.[2] The report of the new English committee[3] is based on the following principles. For **36** elements for which no data have been published since 1919, the values given are taken from Clarke's Recalculation of the Atomic Weights. For certain other elements Clarke's values are modified in view of recent work. For nine "simple" elements, H, He, *C*, N, F, Na, P, As and I, Aston's results with the mass spectrograph are given. The result is a table differing noticeably from recent German and American tables.

On the basis of modern physico-chemical data Moles[4] recalculates eight of the "fundamental" atomic weights.

Boron.—Cousens and Turner[5] find that differences in the density of fused boric oxide with method of preparation are due to internal strain and thus explain those supposed by Briscoe, Robinson and Stephenson to be due to differences in isotopic composition.

Carbon.—Pire and Moles[6] have redetermined the normal density of

THE DENSITY OF CARBON MONOXIDE

	Globe N_3 608.81 ml.	Globe 3 580.49 ml.
	1,25031	
	1.25003	
	1,24998	
	1.25014	1.24995
	1.25009	1.25027
Average	1.25011	1.25011

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[1] *Ber.*, 62B, 1 (1929).

[2] THIS JOURNAL, 51, 647 (1929).

[3] J. *Chem. Soc.*, 216 (1929).

[4] Moles, *Rec. trav. chim.*, *48*,*864* (1929).

[5] Cousens and Turner, J. *Chem. Soc.*, 2654 (1928).

[6] Pire and Moles, *Anales soc. españ. fis. quim.*, 27,267 (1929).

carbon monoxide, made by decomposition of formic acid with concentrated sulfuric acid.

With $(PV)_0/(PV)_1$, 1.00050, and molal volume, 22.414 liters, the atomic weight of carbon is 12.006.

Phosphorus.—Richie[7] gives preliminary values of the density of phosphine at one and at one-half atmosphere as 1.5317 and 0.7622, respectively. Then $(PV)_0/(PV)_1$ is 1.0097 and the atomic weight of phosphorus 30.98.

Chlorine.—Scott and Johnson[7a] prepared nitrosyl chloride by the action of hydrogen chloride on nitrosyl sulfuric acid and purified the product by prolonged fractional distillation in exhausted vessels, with protection from photochemical decomposition. The final product, representing 19 ml. out of an initial 150 ml. was separated by fractionation into seven portions, which yielded percentages of chlorine between 54.235 and 54.079. The three middle fractions were identical in composition and are considered by the authors to represent pure material. Analysis was carried out by comparison with silver. Weights are corrected to vacuum. N = 14.008.

THE ATOMIC WEIGHT OF CHLORINE

Wt. of NOCl	Wt. of Ag	Ratio NOCl: Ag	At. wt. Cl
3 92308	6.46486	0.606832	35.457
4.16219	6.85896	.606825	35.456
4.17839	6.88567	.606824	35.456
	Average	.606827	35.457

Argon.—Baxter and Starkweather[8] have found traces of hydrogen in argon used in a previous density determination. (See report for 1928.) After removal of this hydrogen the purified gas was identical with a new sample which had been freed from hydrogen and purified by fractional adsorption on chilled chabazite.

THE DENSITY OF ARGON

0° P = 760 mm. g = 980.616

Number of adsorptions	Globe IV 2110 95 ml	Globe VIII 3265.23 ml	Globe IX 3210.26 ml.	Average
6		1.78395	1.78381	1,78388
6		1.78399	1.78401	1.78400
7		1,78406	1.78411	1,78408
7		1,78397	1,78402	1.78399
8	1.78391	1,78389		1 78390
8	1 78392	1.78387		1,78389
9	1 78402	1.78404		1,78403
9	1 78396	1.78394		1.78395
Old gas		1.78397		1,78397

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[7] Richie, *Nature*, **123**, 838 (1929).

[7a] Scott and Johnson, J. Phys. **Chem.**, **33**, 1975 (1029).

[8] Raxter and Starkweather, Proc. *Nut. Acad.*, 15, 441 (1929).

THE DENSITY OF ARGON (*Concluded*)

Number of adsorptions	Globe IV 2110.95 ml.	Globe VIII 3265.23 ml.	Globe IX 3210.26 ml.	Average
Old gas		1.78390		1.78390
Old gas		1.78389		1.78389
Old gas		1.78393		1.78393
10		(1.78350)	(1.78374)	
10		1.78395	1.78401	1.78398
11		1.78378	1.78382	1.78380
11		1.78387	1.78391	1.78389
12		1.78390	1.78392	1.78391
14		1.78400	1.78396	1.78398
19	1.78384	1.78389		1.78387
6		1.78401	1.78393	1.78397
Average	1.78393	1.78394	1.78395	1.78394
		P = 506.667 mm.		
	2110.83 ml.	3265.07 ml.	3210.11 ml.	
12		1.18889	1.18884	1.18887
13		1.18889	1.18892	1.18891
15		1.18872	1.18868	1.18870
15		1.18886	1.18884	1.18885
16		1.18880	1.18877	1.18878
17		1.18892	1.18880	1.18886
17		1.18895	1.18890	1.18893
18		1.18874	1.18870	1.18872
20	1.18882	1.18894		1.18888
21	1.18887	1.18896		1.18892
Average	1.18884	1.18887	1.18881	1.18884
		P = 253.333 mm.		
	2110.71 ml.	3264.91 ml.	3209.95 ml.	
13		0.59431	0.59429	0.59430
14		.59426		.59426
16		.59426	0.59427	.59427
19	0.59432	.59428		.59430
20	.59412	.59422		.59417
21	.59419	.59420		.59419
Average	.59421	.59426	0.89428	.59425

From the average densities, weighted inversely as the "average" errors and directly as the pressures, the best straight line to represent change in PV/w with changing pressure is

$$PV/w = 0.560556\ (1 + 0.001068\ (1 - P))$$

From this expression the limiting density of argon is 1.78204 and the atomic weight 39.944 if gram molecular volume is 22.4146 liters. The limiting density is the same as that previously found, but the coefficient of deviation from Boyle's Law is higher, −0.00107 instead of −0.00090.

Nickel.—Baxter and Ishimaru[9] have again compared meteoric with terrestrial nickel, this time by analysis of nickelous bromide. The source

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[9] Baster and Ishimaru, THIS JOURNAL, 51, 1729 (1929).

of meteoric nickel was an iron meteorite suspected to be a fragment from the Cañon Diablo, Colorado, U. S. A., fall. Most of the iron and cobalt had already been removed in an earlier investigation. This material (M) and also common nickel salt (T) were carefully purified and converted into nickelous bromide, and the latter was several times sublimed in a current of hydrogen bromide. The sublimed product was compared with silver in the usual way and the silver bromide determined in most cases. Weights are in vacuum. Br = 79.916.

THE ATOMIC WEIGHT OF NICKEL

	Wt. of $NiBr_2$	Wt. of Ag	Ratio $NiBr_2$:Ag	At. wt. Ni	Wt. of AgBr	Ratio $NiBr_2$:2AgBr	At. wt. Ni
T	4.97931	4.91621	1.012835	58.697	8.55787	0.581840	58.702
T	5.33870	5.27101	1.012842	58.699			
T	7.91596	7.81580	1.012815	58.693	13.60533	.581828	58.698
T	4.63096	4.57242	1.012803	58.690	7.95995	.581783	58.681
T	5.35138	5.28348	1.012851	58.701			
		Average	1.012829	58.696		.581817	58.694
M	6.31054	6.23068	1.012817	58.693	10.84628	.581816	58.693
M	5.66561	5.59419	1.012767	58.683	9.73797	.581806	58.690
M	6.08659	6.00948	1.012831	58.696	10.46106	.581833	58.700
		Average	1.012805	58.691		.581818	58.694
		Average of all		58.694			58.694

The result confirms the evidence obtained with the Sonora, Mexico, meteorite that there is no difference between terrestrial and meteoric material greater than the experimental error.

Copper.—Richards and Phillips[10] have determined the atomic weight of copper from the Calumet and Hecla mines, Lake Superior, U. S. A., and from Chuquicamata, Chili. Both specimens were purified by repeated crystallization of cupric chloride. Attempts to prepare the anhydrous chloride failed. Instead, therefore, both the copper and the chlorine content of solutions of the neutral salt were found. These solutions deposited atacamite, $CuCl_2{\cdot}3CuO{\cdot}4H_2O$, on standing, owing to a small cuprous content of the original cupric chloride. The analysis of solutions from which this deposition had taken place was employed in some instances. In others the deposition was prevented by adding nitric acid, and a correction was applied based on the weight of atacamite deposited from neutral solutions of similar salt.

THE ATOMIC WEIGHT OF COPPER

		Copper, %	Chlorine, %	At. wt. Cu
Lake Superior	Neutral	1.18507	4.02299	63.557
	Acid (corrected)	1.26191	4.28389	63.557
Chuquicamata	Acid (corrected)	1.25088	4.24639	63.557
	Neutral	1.26349	4.28921	63.557
			Average	63.557

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[10] Richards and Phillips, THIS JOURNAL, 51, 400 (1929).

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	Symbol	Atomic Number	Atomic Weight		Symbol	Atomic Number	Atomic 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	74.93	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	12.00	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				

Arsenic.—Krepelka[11] reports the analysis of arsenic trichloride, with the result for the atomic weight of arsenic 74.937. This is slightly lower than the value in general use, 74.96, and is in close agreement with the evidence of the mass spectrograph.

Antimony.—McAlpine[12] has compared samples of antimony from Hungary and Bolivia, by determination of the density of the metal and by titration with potassium bromate, without finding significant differences. This confirms Krishnaswami's work and indicates Muzaffar's conclusion that antimony from different sources varies in isotopic composition to he incorrect. (See reports for 1923 and 1927.)

King and Birge[13] and Birge[14] have obtained spectroscopic evidence of the existence of a small proportion of C^{13} with C^{12}.

Giauque and Johnston[15] find in atmospheric absorption spectra evidence of the occurrence of O^{17} and O^{18} in maximum proportions of 1/10,000 and 1/1250, respectively. If these isotopes are present in ordinary oxygen to the above extent, atomic weights determined with the mass spectrograph by reference to O^{16} may be expected to be about 1/10,000 higher than those found by chemical methods.

Aston[16] from the mass spectrum of lead from Norwegian broggerite has determined its isotopic composition to be as follows:

Pb^{206}	86.8 per cent.
Pb^{207}	9.3 per cent.
Pb^{208}	3.9 per cent.

Since in ordinary lead Pb^{208} is more abundant than Pb^{207}, at least a portion of the latter in the broggerite lead must be the product of radioactive disintegration, and may be the end product of actinium.

The only change in the following table of atomic weights from that published a year ago is the lowering of that of arsenic.

CAMBRIDGE, MASSACHUSETTS

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[11] Krepelka, Nature, 123, 944 (1929).

[12] McAlpine, THIS JOURNAL, 51, 1745 (1929).

[13] King and Birge, Nature, 124, 127 (1929).

[14] Birge, *ibid.*, 124, 182 (1929).

[15] Giauque and Johnston, THIS JOURNAL, 51,3528 (1929); *Naiure,* 123, 831 (1929).

[16] Aston, *ibid.*, 123, 313 (1929).

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

DISSOCIATION CONSTANTS AND HEATS OF IONIZATION OF SOME SIMPLE AMINO ACIDS AND PEPTIDES

BY G. E. K. BRANCH AND S. MIYAMOTO

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Introduction

Owing to their importance in biochemistry and in the theory of amphoterics, the acidic and basic dissociations of amino acids and peptides in aqueous solution have been measured by many investigators. The agreement among their results is not very good, and the values obtained by different investigators are not always comparable as the experiments have been carried out at different temperatures.

We have measured the acidic and basic dissociation constants of glycine, a-alanine, glycylglycine and glycylalanine in aqueous solution at two temperatures, 20 and 0°. Since the change of the logarithm of a dissociation constant with the reciprocal of the absolute temperature is given by the equation $d \ln K/d\,(1/T) = -\Delta H/R$, and since ΔH may be considered as approximately constant over small ranges of temperature, our measurements enable us to express our own values of the dissociation constants and those of other investigators at any one temperature in the neighborhood of room temperature. We have chosen 25° for this purpose. We have also calculated the heats of ionization of the substances acting as acids and bases from our data. Dernby[1] has measured the K_b of glycine and of glycylglycine at two temperatures. The heat of basic dissociation calculated from his results agrees very closely with ours in the case of glycine, but there is a difference of about a thousand calories in the case of glycylglycine. We also believe that calorimetric measurements have been made on some of the amino acids which would permit a calculation of the heats of ionization, but we have not been able to find the data.

Method

The electrometric method was used in determining the dissociation constants. This consists of measuring the PH of solutions of the amphoteric mixed with half an equivalent of hydrochloric acid or of sodium hydroxide by means of a hydrogen electrode balanced against a normal calomel electrode.

Actually the *P*H's of solutions of the amphoterics to which various quantities of hydrochloric acid or sodium hydroxide had been added were measured, and these values of the *P*H were plotted against the number of equivalents of acid or base added. In the figure these titration curves

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[1] Dernby, *Compt. rend. trav. lab. Carlsberg*, 11, 263 (1916).

are shown for the four amphoterics at 20°. The curves obtained at 0° are so similar to those at 20° that they have not been shown.

An acidic or basic dissociation constant can be calculated from any point on such curves. However, it is best to use points which represent the addition of half an equivalent of acid or base to the amphoteric.

At these half-way stages of the titrations the concentrations of the undissociated amphoteric and of its ion are, respectively, $^1/_2\,C - M$, in which C is the total molal concentration of the amphoteric in all its forms and M is the molality of the hydrogen or hydroxide ion. Hence

$$K_a = (\mathrm{H}^+) \times \left[\frac{1}{2}\,C - \frac{Kw}{(\mathrm{H}^+)}\right] \Big/ \left[\frac{1}{2}\,C + \frac{Kw}{(\mathrm{H}^+)}\right] \quad \text{and}$$

$$K_b = \frac{Kw}{(\mathrm{H}^+)} \times \left[\frac{1}{2}\,C - (\mathrm{H}^+)\right] \Big/ \left[\frac{1}{2}\,C + (\mathrm{H}^+)\right]$$

The first of these equations is practically equivalent to the equation $K_a = (\mathrm{H}^+)$, in the case of the substances used by us.

It may be noted that the equilibrium constants obtained in this way are of a hybrid character, for C is a true molal concentration while (H^+) as measured by the hydrogen electrode is an activity.

Results

The P_{H} values at the half titration points and the corresponding acidic and basic dissociation constants are shown in Table I.

TABLE I

VALUES OF P_{H} AT HALF TITRATION. AND DISSOCIATION CONSTANTS

Subs.	Temp., °C.	P_{A} (base added)	K_a	P_{H} (acid added)	K_b
Glycine	0	10.315	4.81×10^{-11}	2.575	2.34×10^{-13}
	20	9.724	1.875×10^{-10}	2.587	1.455×10^{-12}
or-Alanine	0	10.464	3.41×10^{-11}	2.575	2.34×10^{-13}
	20	9.825	1.485×10^{-10}	2.587	1.455×10^{-12}
Glycylglycine	0	8.796	1.6×10^{-9}	3.0925	1.18×10^{-12}
	20	8.254	5.57×10^{-9}	3.121	7.55×10^{-12}
Glycylalanine	0	8.963	1.09×10^{-9}	3.0925	1.18×10^{-12}
	20	8.356	4.41×10^{-9}	3.121	7.55×10^{-12}

These titrations were made by adding 0.1 N acid or base to 0.02 N amino acid or peptide, so that at the half-titration points the total concentration of the organic substance was 0.0182 N.

In all our calculations we have the following values for Kw: 1.005×10^{-14} at 25°, 0.676×10^{-14} at 20° and 0.114×10^{-14} at 0°. The first and last are those given by Lewis and Randall in their book, "Thermodynamics." The value at 20° was obtained from the other two by assuming that $\ln Kw$ is proportional to $1/T$ between 0 and 25°.

Both the ΔH's of dissociation and the equilibrium constants at 25° can be calculated from the results at 20 and 0° by means of the equation

$\ln K_2/K_1 = (-\Delta H/R) \times \Delta(1/T)$. The results of these calculations are shown in Table II.

TABLE II

HEATS OF DISSOCIATION AND EQUILIBRIUM CONSTANTS AT 25°

Substance	K_a	ΔH_a, cal.	K_b	ΔH_b, cal.
Glycine	2.54×10^{-10}	10,700	2.21×10^{-12}	14,600 (14,300)
α-Alanine	2.06×10^{-10}	11,450	2.21×10^{-12}	14,600
Glycylglycine	7.41×10^{-9}	9,830	1.15×10^{-11}	14,800 (16,000)
Glycylalanine	6.025×10^{-9}	11,100	1.15×10^{-11}	14,800

The figures in parentheses are those calculated from Dernby's data

In Table III we have collected most of the published values for the dissociation constants of the four amphoterics discussed in this article. Where necessary we have recalculated the published data so as to obtain the values corresponding to 25°, and to a value of $Kw_{25°} = 1.005 \times 10^{-14}$. In compiling this table we have used to a large extent a collection of the dissociation constant data for all the amino acids and peptides published by P. Kirk and C. Schmidt.[2]

The inner salt theory of amino acids as propounded by E. Q. Adams[3] and N. Bjerrum,[4] throws much light on the electrolytic dissociation of these substances and of the peptides. In this theory glycine is represented by the formula $H_3N^+CH_2COO^-$, and K_a and K_b are considered as hydrolysis constants. Two other constants are obtained by the equations $K^1_a = Kw/K_b$ and $K^1_b = Kw/K_a$. K^1_a and K^1_b are, respectively, the constants of the carboxylic acid, $H_3N^+CH_2COOH$, and of the amine, $H_2NCH_2COO^-$. Both Adams and Bjerrum point out that K^1_a is naturally much greater than K_a for acetic acid, owing to the repulsion of the hydrogen ion by the positive charge. The influence of the nitrogen apart from its positive charge may be assumed to be comparatively small on the basis of its position in the periodic table. In the same way K^1_b might be expected to be markedly greater than the K_b of $H_2NCH_2COOCH_3$.

Bjerrum has pointed out that in the peptides the distance of the positive charge from the carboxyl and that of the negative charge from the amino group is greater than in the amino acids, and that this would account for the fact that the values of K^1_a and K^1_b of the peptides are less than those of the amino acids. The work of Simms[5] confirms this, as he has found that K^1_a and K^1_b of glycylglycylglycine are less then the corresponding constants of glycylglycine.

It may be also noticed that the dissociation constants of the peptides indicate that the influence of a charged group on a dissociation of hydrogen ion is less affected by the intervening atoms than the corresponding

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[2] University of California, *Pub. Physiol.*, [6] *7*, 57-69 (1929).

[3] Adams, THIS JOURNAL, 38, 1503 (1916).

[4] Bjerrum, *Z. physik. Chem.*, **104**, *147* (1923).

[5] Simms, *J.* Gen. *Physiol.*, **11**, 629 (1928).

TABLE III

COMPILATION OF PUBLISHED VALUES OF THE DISSOCIATION CONSTANTS AT 25°

K_a	K_b	Method	Author
		Glycine	
3.4×10^{-12}	2.9×10^{-12}	Conductivity and ester hydrolysis	Winkelblech[10]
[6]2.92×10^{-10}	[6]9.23×10^{-12}	Conductivity	Euler[11]
[6]1.85×10^{-10}	[6]2.52×10^{-12}	Electrometric	Michaelis and Rona[12]
[6]2.20×10^{-10}	[6]2.70×10^{-12}	Electrometric	Sörensen[13]
[6]1.62×10^{-10}	[7]2.44×10^{-12}	Electrometric	Dernby[14]
[6]2.22×10^{-10}	[6]2.70×10^{-12}	Electrometric	Hirsch[15]
1.80×10^{-10}	2.6×10^{-12}	Electrometric	Harris[16]
2.3×10^{-10}	2.14×10^{-12}	Electrometric	Levene, Simms and Pfaltz[17]
2.54×10^{-10}	2.21×10^{-12}	Electrometric	Branch and Miyamoto
		a-Alanine	
9.0×10^{-10}	3.8×10^{-12}	Conductivity and ester hydrolysis	Winkelblech[10]
2.3×10^{-10}	3.1×10^{-12}	Conductivity	Ley[18]
1.8×10^{-10}	2.5×10^{-12}	Electrometric	Harris[16]
[6]2.21×10^{-10}	[6]1.8×10^{-12}	Electrometric	Hirsch[15]
1.91×10^{-10}	2.24×10^{-12}	Electrometric	Simms[19]
$2\text{-}06 \times 10^{-10}$	2.21×10^{-12}	Electrometric	Branch and Miyamoto
		Glycylglycine	
[8]6.98×10^{-9}	[8]1.47×10^{-11}	Electrometric	Eckweiler, Noyes and Falk[20]
2.73×10^{-8}	3.62×10^{-11}	Conductivity	Euler[11]
[6]4.89×10^{-9}	[7]1.45×10^{-11}	Electrometric	Dernby[14]
5.3×10^{-9}	1.4×10^{-11}	Electrometric	Harris[16]
[6]6.54×10^{-9}	[9]8.78×10^{-12}	Electrometric	Levene, Simms and Pfaltz[17]
7.41×10^{-9}	1.15×10^{-11}	Electrometric	Branch and Miyamoto
		Glycylalanine	
5.62×10^{-9}	1.41×10^{-11}	Electrometric	Simms[19]
6.025×10^{-9}	1.15×10^{-11}	Electrometric	Branch and Miyamoto

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[6] Calculated from data obtained at 18°.

[7] Recalculated from data so as to correspond with Kw 25° = 1.005×10^{-14}.

[8] Calculated from results of an electrical titration published by the authors. The authors do not state the temperature, so we have assumed that the measurements were made at 20°.

[9] Calculated from data obtained at 30°.

[10] Winkelblech, *Z. physik. Chem.*, *36*, 546 (1901).

[11] Euler, *ibid.*, **51**, 213 (1907).

[12] Michaelis and Rona, *Biochem. Z.*, 49, 232 (1913).

[13] Sörensen, *ibid.*, **21**, 131 (1909).

[14] Dernby, *Compt. rend. trav. lab. Carlsbsrg*, **11**, 263 (1916).

[15] Hirsch, *Biochem. Z.*, **147**, 433 (1924).

[16] Harris, *Proc. Roy. Soc. London*, **95B**, 440 (1923–1924).

[17] Levene, Simms and Pfaltz, *J. Biol. Chem.*, *61*, 445 (1924).

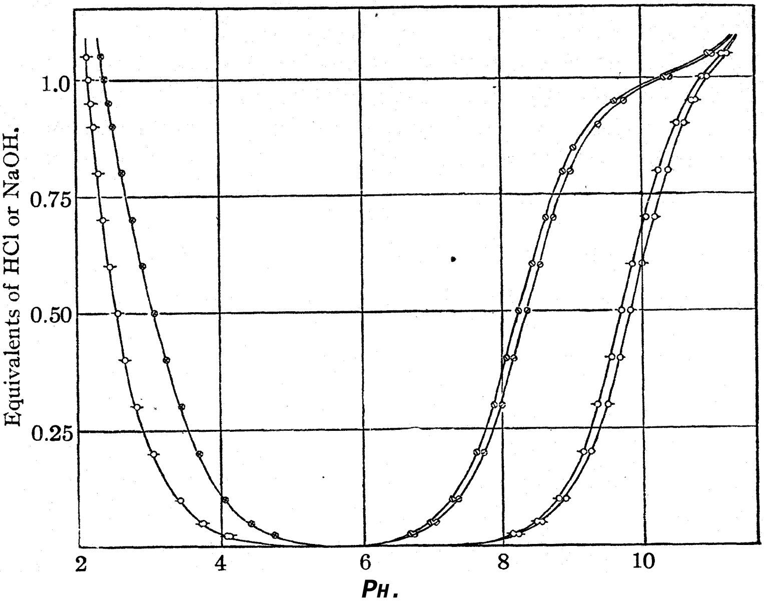
[18] Ley, *Ber.*, **42**, 354 (1909).

[19] Simms, J. *Gen. Physiol.*, **11**, 629 (1928).

[20] Eckweiler, Noyes and Falk, *ibid.*, **3**, 291 (1920–1921).

influence of electrically neutral groups. This may be shown by the following comparisons.

From K_a of acetic acid = $10^{-4.7}$ and K^1_a of glycine = $10^{-2.3}$, the Derrick factor[21] for the $-{}^+NH_3$ group substituted in the a-position may be found to be equal to 1.0. The factor for this group substituted in the δ-position can be obtained from K_a of $C_6H_5CONHCH_2COOH = 10^{-3.66}$ and K^1_a of glycylglycine = $10^{-3.06}$. It is equal to **0.2.** In the case of electrically neutral groups these factors decrease to about one-third of their values for every intervening atom. Thus the factor for α-substituted chlorine is **0.68** and for the same halogen on the 6-atom it is 0.02.[22]



-O, Glycine; O-, a-alanine; 8, glycylglycine; O, glycylalanine; -O-, both glycine and a-alanine; ⊗, both glycylglycine and glycylalanine.

Fig. 1.—Titration curves at 20°.

The results of Schmidt, Appleman and Kirk[23] on a-, β-, y-, 8-amino substituted propionic and valeric acids show the same phenomenon. Thus for the series a-aminovaleric acid, β-aminopropionic acid, γ-aminovaleric acid and 6-aminovaleric acid, $K^1_a = 10^{-2.4}, 10^{-3.6}, 10^{-4.0}$ and $10^{-4.2}$. The Derrick factors for the $-{}^+NH_3$ group in the a-, β-, γ- and 6-positions,

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[21] Since $H_3N^+CH_2COOH$ is a fairly strong acid, the use of the Derrick factor is to be preferred to a direct comparison of the logarithms of the dissociation constants.

[22] In Derrick's paper the influence of COOH appears to be persistent, but this is because the dissociation constants of symmetrical dibasic acids should be divided by two before they are compared with those of monobasic acids.

[23] Schmidt, Appleman and Kirk, J. *Biol. Chem.*, **81,** *723* (1929).

calculated from these results, are 1.0, 0.33, 0.2 and 0.14, respectively. The corresponding values for chlorine are 0.68, 0.19, 0.06, 0.02.[24]

This persistence of the influence of charged groups on dissociation constants is also shown by the fact that K^1_a and K^1_b of glycylglycine are noticeably greater than those of glycylglycylglycine. Another example of this generalization is that in the case of the dibasic saturated acids the first dissociation constants are almost exactly twice and the second are markedly less than one-half the dissociation constants of the corresponding fatty acids, when there are four or more atoms between the two carboxyl groups.

In their experiments the authors noted that alanine reacted like glycine and that glycylalanine like glycylglycine when these substances were treated with acid, but that this was not the case when base was added. Although the results of other investigators do not confirm this observation, it is shown so clearly in Fig. 1 and was equally apparent in the titration curves obtained at 0° that the authors believe that it is valid.

Summary

The acidic and basic dissociation constants of glycine, α-alanine, glycylglycine, and of glycylalanine were measured at two temperatures, 20 and 0°, by the electrometric method.

From these measurements the heats of acidic and basic dissociations of these amphoterics were calculated.

These values were used to calculate the dissociation constants at 25°.

The available data on the dissociation constants of these substance are collected together and where necessary the results have been extrapolated to 25°.

The authors note that the dissociation constants of these substances indicate that the influence of electrically charged groups on dissociation constants is not lessened to the same extent by intervening groups as is that of electrically neutral groups.

The authors' results indicate that an a-substituted methyl group influences the reaction of these substances with base to a much greater extent than their reaction with acid. This is not confirmed by the work of others in this field.

BERKELEY, CALIFORNIA

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[24] **Derrick,** THIS JOURNAL, 33, 1167 (1911).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CINCINNATI]

THE ETHYL ACETATE EQUILIBRIUM. II.[1]

BY R. C. CANTELO AND R. D. BILLINGER

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The ethyl acetate equilibrium is represented by the chemical equation $C_2H_5OH + HAc \rightleftharpoons C_2H_5Ac + H_2O$; and the equilibrium constant for the system is given by $K_a = a_3a_4/a_1a_2$ where $a_1, a_2, \ldots$ are the activities of the ethyl alcohol, acetic acid,. . . . . in the system. In the absence of salts, K_a for this system is considered to be equal to K_E, where $K_E = C_3C_4/C_1C_2$, and $C_1, C_2, \ldots$ are the molar concentrations.

Poznanski[2] states that Guldberg and Waage's[3] as well as van't Hoff's[4] determinations of the equilibrium constant K_E as calculated from the data of Berthelot and de Saint Gilles for this equilibrium are inaccurate. He states that Schwab[5] found K_E to vary from 1.0 to 6.8. Poznanski found experimentally that if varying quantities of acid are added to a mixture of alcohol and water, K_E varies on both sides of the value **3.79,** which he found when 1 mole of acid + 1 mole of alcohol was used as the initial system.

We have throughout our experiments kept the proportions of acid, alcohol and water constant, so that for our purpose, namely, to discover the effect of the addition of salts upon K_E, we are justified in writing $K_a = K_E$ in the absence of salts. However, when salts are present, K_E is no longer equal to K_a. K_a is a true *constant* and is related to K_E by the expression $K_a = K_E\Sigma f_{C_2H_5OH}$, where f is the activity coefficient; f for a given species, in the presence of salts, is a function of the ionic strength of the electrolytes present."

In a'previous paper[7] we have reported the effects of the salts sodium chloride, sodium iodide and sodium thiocyanate upon the equilibrium constant, K_E, of the ethyl acetate equilibrium. The present communication contains the results which we have obtained by the use of the salts sodium bromide, sodium acetate and sodium nitrite. It includes also the results of our study of the reaction rate constants for this system in the presence of the six salts cited.

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[1] This paper and a previous one published under the same title represent an abstract of the thesis submitted by R. D. Billinger to the Graduate School of the University of Cincinnati, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Poznanski, *Roczniki Chem.*, 8,377 (1928); *C. A.*, 23,1559 (1929).

[3] Guldberg and Waage, *J. prakt. Chem.*, 19, 69 (1879).

[4] Van't Hoff, *Ber.*, 10, 669 (1877).

[5] Schwab, *Rec. trav. chim.*, 2, 46 (1883).

[6] Debye and McAuley, *Physik. Z.*, 26, 22 (1925).

[7] Cantelo and Billinger, THIS JOURNAL, 50,3212 (1928).

The general procedure in measuring the values of K_E is given in our first paper. The results obtained with the new series of salts are given in Tables I, II and III; the results for the complete series are shown graphically in Fig. 1. The salt concentration given is the molar concentration in the initial mixture used. The proportions of ethyl alcohol, acetic acid and salt solution were the same as those reported in our previous paper. The temperature was 78°.

TABLE I

EFFECT OF SODIUM BROMIDE:

Salt concn.,	Sample	K_E	Av. K_E	Σf
0	A	3.686	3.705	1
0	B	3.725		
0.096	A	4.059	4.068	0.91
	B	4.077		
.191	A	4.094	4.103	.90
	B	4.111		
.289	A	4.254	4.256	.87
	B	4.257		
.382	A	4.461	4.480	.83
	B	4.499		

TABLE II

EFFECT OF SODIUM ACETATE

Concn.	Sample	K_E	Av. K_E	Σf
0.097	A	3.488	3.477	1.07
	B	3.466		
1.90	A	3.556	3.552	1.04
	B	3.547		
.283	A	3.604	3.604	1.03
	B	3.605		
.376	A	3.621	3.652	1.02
	B	3.683		

TABLE III

EFFECT OF SODIUM NITRITE

Concn.	Sample	KE	Av. KE	Σf
0.093	A	3.648	3.640	1.02
	B	3.632		
.184	A	3.752	3.710	1.00
	B	3.668		
.279	A	3.829	3.779	0.98
	B	3.729		
.367	A	3.976	3.924	0.95
	B	3.871		

Discussion of Results

The curves in Fig. 1 show how K_E increases with increasing salt concentration. Each salt has its own specific effect; and the salts sodium nitrite and sodium acetate *apparently* depress the equilibrium constant below the value 3.7. It is obvious, however, that in the case of sodium nitrite the reaction $NaNO_2 + HAc \quad KAc + HNO_2$ occurs; and our titration values really give the *total* acid present. We had evidence of the complications arising in the case of this salt in the fact that a considerable pressure developed and a number of filled tubes broke in heating. For this reason the results for this salt must be regarded merely as approximations to the true values.

The variation in K_E due to the presence of dissolved salts arises from the effects of these salts upon the activity coefficients of the reacting species in the equilibrium mixtures. The stoichiometrical concentrations are different in the final mixtures, but the ratio a_3a_4/a_1a_2 is a constant always. Again, even though $a_1, a_2 \ldots$ are not always the same in the final mixtures, the above ratio must always be constant, on account of the relation $\bar{\mu}_1 + \bar{\mu}_2 = \bar{\mu}_3 + \bar{\mu}_4$, which holds for chemical equilibrium, where $\bar{\mu}$ is the molecular chemical potential. Any change in a potential of the left-hand member must be accompanied by a compensating change in the right-hand member. The relation between a, the activity, and C, the molar concentration, is given by $a = fC$; f varies with the nature of the thermodynamic environment.

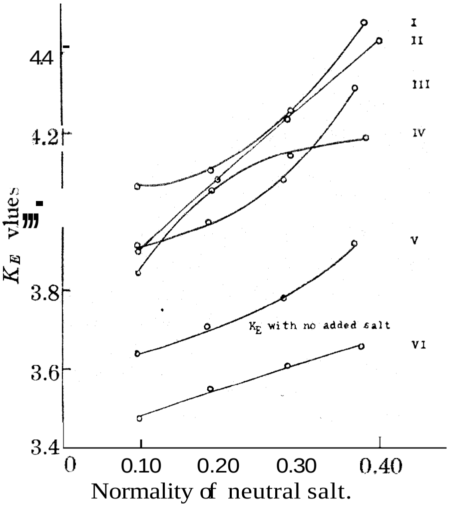

Fig. 1—K_E values: I, NaBr mixtures; II, NaCl; III, NaCNS; IV, NaI; V, $NaNO_2$; VI, $NaC_2H_3O_2$.

Determination of Reaction Velocity Constants.—The velocity of the reaction $C_2H_5OH + HAc \rightleftharpoons C_2H_5Ac + H_2O$ is given by the relation, $V = k'f_1f_2C_1C_2 - k''f_3f_4C_3C_4$, where f and C are the activity coefficient and molar concentration, respectively, at any instant, of a given species, and k' and k'' are constants; f may be expressed as a function of μ, the ionic strength,[6] $\log f = \mu k$, or $f = e^{\mu k}$. Hence, for V we can write

$$V = k'\, e^{\mu(k_1 + k_2)}\, C_1C_2 - k''\, e^{\mu(k_3 + k_4)}\, C_3C_4$$

Unfortunately, we do not know the values of k_1, k_2—, so that we are unable to use the above equation directly for the determination of k' and k''. We are forced, therefore, to use the classical expression for V, namely

$$V = k_1C_1C_2 - k_2C_3C_4$$

and to calculate k_1 and k_2 solely by an application of mathematics, and then to attempt a determination of the true values of k' and k''.

For the reaction $C_2H_5OH + CH_3COOH \quad CH_3COOC_2H_5 + H_2O$, let a, b, c and d denote the initial concentrations in moles per liter of alcohol, acid, ester and water, and let the amount of change after the time t be x. The velocities of the direct and reverse reactions are

$$\frac{dx_1}{dt} = k_1(a - x)(b - x), \frac{dx_2}{dt} = k_2(c + x)(d + x)$$

hence the velocity of esterification is

$$\frac{dx}{dt} = k_1(a - x)(b - x) - k_2(c + x)(d + x)$$

This equation may be integrated, giving, finally, the expression

$$k_2 = \frac{1}{t} \cdot \frac{K - 1}{P} \log \frac{(Q - P)[Q + P - 2(K - 1)x]}{(Q + P)[Q - P - 2(K - 1)x]}$$

where K is the equilibrium constant, defined by $K = k_1/k_2$

$$P = \sqrt{Q^2 - 4(K - 1)(Kab - cd)} \text{ and } Q = [K(a + b) + (c + d)]$$

Experimental Method

The general procedure was similar to that described under the determination of K_E. Since the reaction rate is slow at room temperature, the actual starting time was not taken until the mixtures were sealed in tubes and the tubes immersed in boiling carbon tetrachloride. The time of stopping was taken when the tubes were withdrawn from the heating flask and immersed in ice water, prior to titration of the acetic acid present. Thus the time recorded in the tables represents the time during which the samples were at the temperature of boiling carbon tetrachloride.

The proportions of ethyl alcohol, acetic acid and salt solution in the initial mixture were the same as in the equilibrium experiments.

The values of k_2 for the reaction were calculated from the data obtained by the use of the equation given above. For K in that equation we substituted the determined value K_E for the salt concentration used. However, the ratio k_1/k_2 is probably not constant, so that the values given in Table V are the averages of the *last three measurements* only. In Table IV, however, we give complete values for two series, in order to show the trend of the values of k_2. We found this trend in all our series.

TABLE IV

REACTION VELOCITY CONSTANTS IN PRESENCE OF 0.200 *N* SODIUM CHLORIDE AND OF 0.298 *N* SODIUM THIOCYANATE

0.2 *N* Sodium chloride Time, minutes	k_2	0.3 N Sodium thiocyanate Time, minutes	la
73	0.000261	98	0.000181
138	.000228	137	.000119
198	.000222	174	.000116
230	.000221	263	.000113
288	.000215	297	.000105
408	.000186	329	.000108

TABLE V

THE EFFECT OF VARIOUS SALTS UPON THE VELOCITY CONSTANT k_1 (TEMP., 78°)

$k_1 \cdot 10^4 = k_2.\text{detd. } K_E \cdot 10^4$

Salt concn.	NaCl	NaCNS	NaI	NaBr	NaAc	$NaNO_2$
0.1	6.16	4.25	5.23	6.58	0.643	0.668
.2	8.46	4.43	5.75	8.39	.671	.529
.3	10.06	4.41	6.83	10.83	.623	.753
.4	10.90	5.20	5.83	12.75	.623	.531

0.00 **salt gave** $k_1 \times 10^4 = 3.86$. 0.02 HCl **gave** $k_1 \times 10^4 = 29.19$.

The results are shown graphically in Fig. **2.**

Discussion of Results

The effects of the anions in increasing the reaction velocity seem to be almost in the same order as that indicated in the displacement of equilibrium, except that here the iodide ion seems to have a greater effect than the thiocyanate ion.

The explanation of the cause of the increased velocities, that is, the catalytic effect, might be attempted in terms of various theories. These theories may be summarized briefly as follows: (1) increased hydrogen-ion concentration,[8] (2) hydration of salt with resulting increase in hydrogen-ion concentration[9] (Manning's work,[10] however, seems to show that hydration of solute does not affect the reaction rate constants), (3) increased activity of hydrogen ion,[11] and of hydrogen ion and of the undissociated molecule,[12] (4) shift in the water equilibrium;[13] this amounts to a change in solvent, in which concentrations, reaction velocities, ionization, etc., will he different from those in the original solvent, (5) the activity theory of reaction rate,[14] (6) Brönsted's theory of reaction velocity,[15] (7) change in the thermodynamic potential caused by a change in the field surrounding the reacting substances.[16]

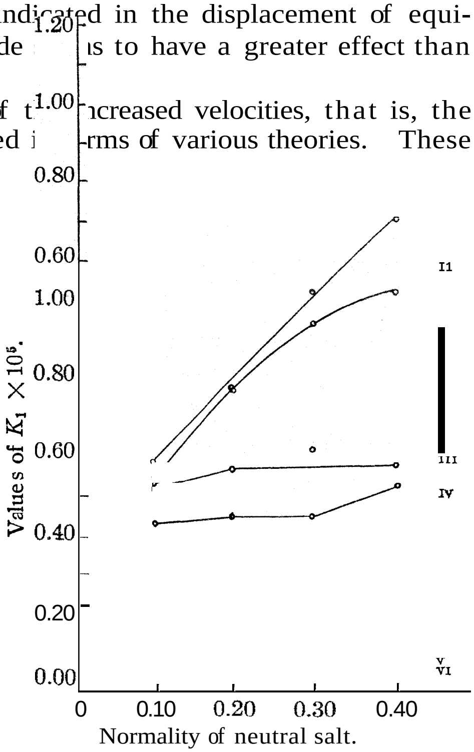

Fig. 2.—Reaction rate curves: I, NaBr mixtures; II, NaCl; III, NaI; IV, NaCNS; V, $NaC_2H_3O_2$; VI, $NaNO_2$.

This last is substantially the hypothesis we have used in our investigation. We believe that the effect of salts upon equilibrium and velocity constants is due to changes in the activity coefficients of the reacting substances. This change itself is due to the new thermodynamic environment of the reacting substances in the presence of salts.

[8] Arrhenius, *Z. physik. Chem.*, 31, 197 (1899); Euler, *ibid.*, 32,348 (1900).

[9] Wilson, THIS JOURNAL, 42,715 (1920).

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

[11] Åkerlöf, *Z. physik. Chem.*, *98*, 260 (1921).

[12] Taylor, THIS JOURNAL, 37, 551 (1915).

[13] Bancroft, *J. Phys. Chem.*, 30, 1194 (1926); Bowe, *ibid*, 31, 291 (1927).

[14] Harned and Seltz, THIS JOURNAL, 44,1476 (1922).

[15] Bronsted, *Z. physik. Chem.*, 102, 169 (1922).

[16] Acree, THIS JOURNAL, 41,474 (1919).

Most other investigators of the influence of salts upon rates of esterification have used hydrochloric acid as well; and the increased velocity has been attributed to the increase in hydrogen-ion concentrations. Our investigations were carried out in the absence of mineral acid, so that if the presence of salts varied the hydrogen-ion concentration or activity, it was the hydrogen-ion concentration or activity resulting from the reaction mixture—acetic acid, ethyl alcohol and water.

Using our determined values for k_1 and k_2, we may write

$$V = k_1C_AC_B - k_2C_EC_F \tag{1}$$

and also we may write

$$V = k'C_AC_Bf_Af_B - k''C_EC_Ff_Ef_F$$

Then equating coefficients of like terms, we have

$$k_1 = k'f_Af_B;\ k_2 = k''f_Ef_F \text{ or}$$
$$\log k_1 = \log k' + \log f_A + \log f_B, \text{ etc.}$$

If we assume that the Debye–McAuley relation holds for this system, we have

$$\log k_1 = \log k' + \mu k_A + \mu k_B$$
$$\log k_1 = \log k' + m\mu$$

where m is a constant.

We may test this relation by plotting $\log k_1 + 5$ against μ, which is here equal to C, the molar salt concentration. Such a plot is given in Fig. 3. Omitting entirely the plot for sodium nitrite, it is seen that the points fall approximately upon straight lines. While the points for sodium acetate fall very well upon a straight line, yet this line does not tend toward the same log k_1 value for zero concentration as do the others. It is evident that a secondary salt effect has come into play in this case.

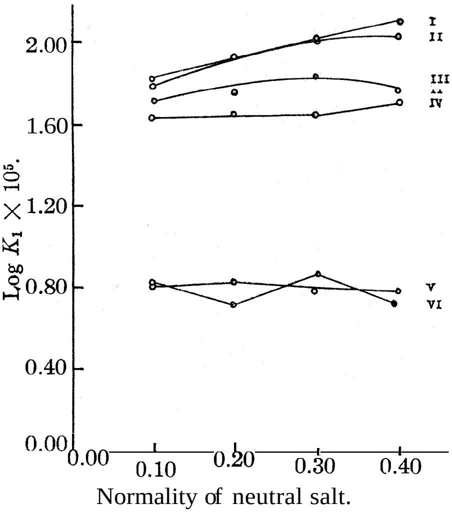

Fig. 3.—I, NaBr mixtures; II, NaCl; III, NaI; IV, NaCNS; V, $NaC_2H_3O_2$; VI, $NaNO_2$.

Extrapolation to zero concentration of added salt gave the following values

For sodium bromide, 0.000537
For sodium chloride, 0.000457
For sodium iodide, 0.000467
For sodium thiocyanate, 0.000437

These values are somewhat higher than the value 0.000386 obtained for k' in the absence of salts.

We hope to continue the investigation in the region 0.10 to zero ionic strength of the four salts mentioned above, and also to extend the study to salts of higher valence type. At the same time we are planning a study of the effect of the six salts upon the activity of the hydrogen ion of water and of acetic acid.

Summary

The relation between the true equilibrium constant, K_a, for the ethyl acetate equilibrium in the presence of salts, and the constant K_E calculated from the classical mass action expression is $K_a = K_E \Sigma f_1$, where f is the activation of a given reacting species. The term Sf varies with the salt present, giving rise to different values of K_E.

The value of K_E has been determined in the presence of the salts sodium bromide, sodium acetate and sodium nitrite. The values for sodium nitrite as added salt are considered to be only approximate. The value of K_E increases with the concentration of added salt. With sodium acetate as added salt, K_E is less than the value obtained in the absence of salts, and K_E increases linearly with the concentration of sodium acetate.

The velocity constants for the reaction have been determined by means of an expression which contains K_E, the determined equilibrium constant for the specific salt, and specific concentration. Values are reported for the specific reaction rates for the forward action for six salts. The values reported are those in the neighborhood of equilibrium where $K_E = k_1/k_2$.

The order of the effects of the salts upon the velocity of reaction is almost the same as that indicated in the displacement of equilibrium. The specific reaction rate is practically constant for all concentrations of sodium acetate. A secondary salt effect evidently occurs with sodium acetate, so that its effect cannot be interpreted in the same way as can the effects of the salts sodium iodide, bromide, chloride and thiocyanate.

The Debye–McAuley relation for the activity of non-electrolytes has been used to obtain an equation for the rate of the esterification reaction. This equation has been combined with the classical expression to obtain a relation to test the validity of the former equation. It has been shown that this equation is in substantial agreement with the experimental data.

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[CONTRIBUTION NO. 617 FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

NEUTRAL SALT ACTION. THE RELATIVE INFLUENCE OF CATIONS AND ANIONS UPON THE EQUILIBRIUM $2\mathrm{Fe(CN)_6}^{---} + 3\mathrm{I}^- \rightleftarrows 2\mathrm{Fe(CN)_6}^{----} + \mathrm{I_3}^-$[1]

BY VICTOR K. LA MER AND HAROLD B. FRIEDMAN

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I. Introduction

In a recent paper La Mer and Sandved[2] studied the variation in the stoichiometric equilibrium constant, K_c', corresponding to the reaction

$$2\mathrm{Fe(CN)_6}^{---} + 3\mathrm{I}^- \leftrightarrows 2\mathrm{Fe(CN)_6}^{----} + \mathrm{I_3}^-$$

when the system was prepared entirely from potassium salts, with and without addition of potassium chloride. They showed that it was only in the presence of a considerable excess of the foreign neutral salt that constant values for the mass action constant, K'_c could be obtained with varying initial concentrations of potassium ferricyanide and potassium iodide, for any given salt environment.

The purpose of the present paper is to extend these studies to a consideration of the influence of substituting sodium for potassium as cation, and additions of chlorides, nitrates and sulfates in the form of the potassium or sodium salts, to determine whether any marked difference of behavior occurs. Since the reaction involves only ions of negative sign, it seemed reasonable to expect that specific behavior might perhaps be restricted primarily to changes in the nature of the cations and be essentially independent of the nature of the anion, in accordance with Bronsted's theory of specific interaction, even though the concentrations employed exceed the region for which this theory was proposed and verified, namely, at 0.1 N concentrations.[3,4,5]

In view of the renewed interest in the question of the existence of tri-iodides in solution, the data will be considered from two view-points; namely, (a) poly-iodide formation denied, and (b) tri-iodide formation accepted.

II. Experimental Method

The experimental method employed was similar in essentials to that of La Mer and Sandved[6] except that no attempt was made to follow quan-

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[1] Paper presented at the Columbus (April, 1929) Meeting of the American Chemical Society. (Original manuscript received November 10, 1928.)

[2] La Mer and Sandved, THIS JOURNAL, 50, 2656 (1928).

[3] (a) Bronsted, *ibid.*, 44, 877 (1922); (b) *ibid.*, 45, 2898 (1923).

[4] Güntelberg, Z. *physik. Chem.*, 123, 199 (1926).

[5] (a) La Mer and Cook, THIS JOURNAL, 51, 2622 (1929); (b) La Mer and Goldman, *ibid.*, 51, 2632 (1929).

[6] Ref. 2, p. 2658.

titatively the rate of attainment of equilibrium. Weighed amounts of the desired salts, potassium ferricyanide, potassium or sodium iodide, and added neutral salt, were dissolved in boiled distilled water in a flask calibrated to contain 100 cc. at 25°. The volume was adjusted to the mark and the flask placed in a thermostat at 25 ± 0.005°, where the mixture was left for three hours to attain equilibrium. That true equilibrium was reached in this time was demonstrated by the fact that no further change occurred in samples allowed to remain in the bath for a longer time.

Six portions of approximately 0.05 N sodium thiosulfate solution were weighed out from a weight buret into 500-cc. stoppered Erlenmeyer flasks and diluted to 125 cc. with boiled water. At equilibrium, samples from the reaction flask in the bath were withdrawn with a 10-cc. pipet; 2 cc. of 1% starch solution was added to a portion of the thiosulfate, and then the sample added dropwise from the pipet, which was calibrated in 1/10 cc., permitting readings to 1/100 cc. The sample was added with shaking until a definite color change corresponding to a minute excess of free iodine was produced.

The several factors contributing to the accuracy of this method and its preference over others have been discussed previously. The presence of ferri- and ferrocyanides introduces some difficulty in reading the end-point, since the blue color of starch–iodide appears green in the yellow solution. That this difficulty was overcome by titrating with color standards in a good light is evidenced by the constancy of the ratios of the 6 titers, g. thiosulfate/cc. sample used, whose average value was taken as that for the experiment. The separate ratios, however, generally differed by but several parts per thousand, and the average deviation from the mean considerably less, as shown in the following typical examples.

RATIO, G. $Na_2S_2O_3$/CC. SAMPLE USED

	Expt. 9 Poorest agreement accepted		Expt. 18 Average agreement		Expt. 17 Best agreement
	(0.2879) (discarded)		(0,3532) (discarded)		0.1110
	.2751		.3504		.1112
	,2751		.3502		.1118
	.2724		.3502		.1118
	.2716		.3494		.1110
	.2740		.3500		.1112
Av.	.2736	Av.	.3500	**Av.**	.1113

The titration values for comparable experiments are slightly higher in this than in the previous paper, which we believe to be due to a constant personal error in determining the color standard corresponding to the first permanent appearance of iodine.

The salts used were all of C. P. grade and were twice recrystallized, except the sodium and potassium iodides, which gave no tests for iodine. The thiosulfate solution was restandardized at intervals of two weeks.

Considerable difficulty was encountered in weighing out the sodium iodide, owing to its hygroscopic properties. For that reason the results with sodium salts may not be as accurate as when potassium iodide was used.

III. Data

Table I shows the results of the investigation, the amounts and characters of the added neutral salts being given in Cols. 3 and 4. Column 5 gives the ionic strength, μ, of the systems, and Col. 6 gives x, the *equivalents of titratable iodine* in a liter of the reaction mixture; x is also the moles/liter of the ferrocyanide formed at equilibrium.

It will be noted that when potassium salts are added, the only cation present is the potassium ion, except in Expt. 4. In the case of sodium salts, unfortunately, sodium ferricyanide of sufficient purity was not available at the time, so the potassium ferricyanide was used throughout. The experiments with sodium salts, therefore, contain 0.225 molar potassium ion as cation. This amount of potassium ion is practically insignificant compared to the large amount of sodium ion present, ranging

TABLE I

SHOWING THE INFLUENCE OF ADDED NEUTRAL SALTS ON THE STOICHIOMETRIC EQUILIBRIUM CONSTANT K'_c AND K_c^{∞} AT 25°

a = initial concn. of $Fe(CN)_6^{---}$ = 0.075 M $K_3Fe(CN)_6$ (K salt in all cases). b = initial concn. of I^- = 0.20 M KI or NaI as indicated in Col. 2. L_c was taken as 0.00611 *(see* previous paper)

Expt.	b	Concn. of added salt, m./l.	Added salt	μ	$x \times 10^3$	$C_{I_3^-} \times 10^3$	$K'_c \times 10^3$	$K_c^{\infty} \times 10^3$
1	K	...	.....	0.65	3.356	1.626	0.481	0.0952
2	K	1.0	KCl	1.65	6.743	3.265	4.65	0.881
3	K	2.0	KCl	2.65	9.978	4.831	17.9	3.25
4	K	1.0	NaCl	1.65	5.823	2.822	2.85	0.547
5	K	1.0	$NaNO_3$	1.65	5.497	2.661	2.36	0.454
6	K	0.5	K_2SO_4	2.15	5.954	2.885	3.07	0.588
7	Na	1.0	NaCl	1.65	5.708	2.768	2.67	0.513
8	Na	2.0	NaCl	2.65	8.735	4.228	11.2	2.074
9	Na	3.0	NaCl	3.65	12.27	5.935	37.8	6.656
10	Na	2.0	$NaNO_3$	2.65	7.744	3.751	7.42	1.389
11	K	3.0	KCl	3.65	12.89	6.237	45.4	7.935
12	K	1.0	KNO_3	1.65	6.002	2.908	3.15	0.603
13	K	2.0	KNO_3	2.65	8.115	3.929	8.70	1.622
14	K	3.0	KNO_3	3.65	9.479	4.589	14.9	2.733
15	Na	3.0	$NaNO_3$	3.65	9.578	4.637	15.5	2.830
16	K	3.0	KNO_3	3.65	9.577	4.636	15.5	2.830
17	Na	0.5	Na_2SO_4	2.15	4.976	2.411	1.70	0.330
18	K	4.0	KCl	4.65	15.69	7.585	96.2	16.17
19	Na	4.0	NaCl	4.65	13.84	7.191	64.2	10.22

from 1.2 to 4.2 molar, so that we may for all practical purposes regard the cation as entirely sodium. The influence of interchanging 0.2 M of K^+ for 0.2 M Na^+ when $\mu = 1.65$ can be seen by comparing the values of K'_c in Table I for Expts. 4 and 7, where the systems are otherwise identical. K'_c is reduced from 2.85 to 2.67, or 6.5%.

IV. The Equilibrium Constants K_c and K'_c

Since the only quantity subject to direct experimental measurement is x, *the number of equivalents of iodine at equilibrium,* we are at liberty to consider this iodine as existing either (a) entirely as molecular iodine or (b) as a mixture of tri-iodide ion and molecular iodine in equilibrium, according to one's preference regarding the question of the existence of tri-iodides. The constants which can be calculated may be derived as follows. Consider the reactions

$$2Fe(CN)_6^{---} + 21^- \leftrightarrows I_2 + 2Fe(CN)_6^{----} \qquad (1)$$

$$I_2 + I^- \leftrightarrows I_3^- \qquad (2)$$

$$2Fe(CN)_6^{---} + 3I^- \leftrightarrows I_3^- + 2Fe(CN)_6^{----} \qquad (3)$$

where **(3)** is the sum of (1) and (2). The various concentrations in *moles* per *liter* may be represented

Initially	**At equilibrium**
$c_{Fe(CN)_6^{---}} = a$	$c_{I^-} = y \quad c_{I_3^-} = z \quad c_{I_2} = w$
$c_{I^-} = b$	$c_{Fe(CN)_6^{---}} = (a - x)$ *and* $c_{Fe(CN)_6^{----}} = x$

since one mole of ferrocyanide is formed for each atom of iodine.

Since in tri-iodide ion only two of the iodine atoms are titratable with thiosulfate, we have

$$x = 2w + 2z \qquad (4)$$

Counting the total number of atoms of iodine

$$y + 3z + 2w = b \qquad (5)$$

The mass action law for Reaction 2 gives

$$L_c = \frac{c_{I_2} \times c_{I^-}}{c_{I_3^-}} = \frac{wy}{z} \qquad (6)$$

Solving (4) and *(5)* for z and w, we find

$$\begin{aligned} z &= b - x - y \\ w &= 3/2x + y - b \end{aligned} \qquad (7)$$

Substituting z and w from (7) and (6) and solving the resulting quadratic in y

$$y = 1/4\ (2b - 2L - 3x \pm \sqrt{(2b - 2L - 3x)^2 + 16L(b - x)}) \qquad (8)$$

The mass action law for Reaction 1 gives under assumption (b)

$$K_c = \frac{wx^2}{(a - x)^2y^2} \qquad (9)$$

and for Reaction **3** under assumption (b)

$$K'_c = \frac{zx^2}{(a - x)^2y^3} \qquad (10)$$

(10) differs from (9) only by the factor L, since

$$\frac{K_c}{K'_c} = \frac{wy}{z} = L$$

when the values for y are taken from (8). The experimental data have been substituted in (10) and the corresponding constants recorded in Col. 8 of Table I. Since the initial c_{I^-} was constant in all of our experiments, it is impossible to determine the relative merits of assumptions (a) or (b). However, when we examine the data of La Mer and Sandved, an extract of which is given in Table II, along with computations for K_c^{∞} (see below), we see that although K', is an excellent constant for each environment, the corresponding values for K_c^{∞} (tri-iodide formation ignored, *i*. e., L taken as equal to ∞) drift by 33%.

TABLE II

DATA OF LA MER AND SANDVED

Expt.	a = init. $c_{\mathrm{K_3Fe(CN)_6}}$	b = init. c_{KI}	Added KCl, m./l.	μ	$K'_c \times 10^3$	$K_c^{\infty} \times 10^3$
			Constant Environment I			
5–6–7 (Av.)	0.075	0.20	1.00	1.65	4.49	0.852
8	.075	.175	1.025	1.65	4.43	.737
9	.075	.15	1.05	1.65	4.45	.641
			Constant Environment II			
12	.10	.25	0.825	1.675[a]	4.44	1.03
13	.10	.20	.875	1.675	4.42	0.824
			Constant Environment III			
16	.05	.20	1.075	1.575	4.48	.868
17	.05	.15	1.125	1.575	4.51	.662

[a] The μ values (Col. 5) for Expts. 12–15 inclusive of La Mer and Sandved's Table I were erroneously recorded as 1.625 instead of 1.675. The value for K'_c should read 0.199×10^{-1} instead of 0.199×10^{-3}. The last column in Table I should read 10 X K'_f instead of K'_f; *i. e.*, one decimal place was omitted.

Thus the assumption made (but not proved) in the previous paper that one must postulate the existence of tri-iodide ions in order to obtain a mass action constant for a solution of constant environment except for small changes in iodide concentration is fully justified and should assist in removing any doubts which may still persist about the validity of this assumption.[7]

If one desires to find the limiting value of the ratio K_c^{∞}/K'_c in order to see the relation between these two constants, he may proceed in the following way.

From (6), $z = 0$ when L is set equal to infinity, and from (4) and (5)

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[7] This question was revived with much interest at the Detroit (September, 1927) and Swampscott (September, 1928) meetings of the American Chemical Society, Professor W. D. Bancroft contending that potassium tri-iodide does not exist at 25°.

w = $x/2$ and y = b-x, whence (11) is derivable from (10) by substitution. Call

$$K_c^\infty = \frac{x^3}{2(a-x)^2(b-x)^2} \tag{11}$$

as *the constant* for Reaction *1* under assumption (a), *i.* e., K_c^∞ is the limit of K_c as L $\longrightarrow \infty$. Now let us calculate approximate expressions for y, z, w and K_c^∞, under the assumption that L is small in comparison to b, which is true when we set b = 0.2 M as in the present experiments.

From the identity[8]

$$(2b - 2L - 3x)^2 + 16L(b-x) = (2b + 2L - 3x)^2 + 8Lx$$

we find, extracting the square root to the right by the binomial theorem, and retaining two terms only

$$\sqrt{(2b - 2L - 3x)^2 + 16L(b-x)} = 2b + 2L - 3x + \frac{4Lx}{2b + 2L - 3x} \tag{12}$$

and with the same degree of accuracy, we may replace the expression to the right by 2b + 2L—$3x$ + $(2Lx/b)$. Substituting in (S), we find

$$y \cong b - \frac{3}{2}x + \frac{Lx}{2b} \tag{13}$$

whence by (7)

$$z \cong \frac{1}{2}x - \frac{Lx}{2b} \tag{14}$$

$$w \cong \frac{Lx}{2b}$$

Substituting (13) and (14) in (10), it is seen that

$$K'_c \cong \frac{x^3[1 - (L/b)]}{2(a-x)^2(b - 3/2x)^3} \tag{15}$$

since $Lx/2b$ is negligible in (13).

Dividing (12) by (15)

$$\frac{K_c^\infty}{K'_c} \cong \frac{(b - 3/2x)^3}{(1 - L/b)(b-x)^2} \tag{16}$$

or performing the division and retaining only terms of the first degree in L and x

$$\frac{K_c^\infty}{K'_c} \cong b + L - \frac{5}{2}x \tag{17}$$

which is of the order of magnitude of b, since L and x are small in comparison to b in these experiments. The reader may verify relation (17) by dividing Col. 9 by Col. 8 in Table I. It will be noted that the ratio is sensibly equal to b = 0.2. That is, one may compute K', with sufficient accuracy for most purposes directly from K_c^∞ values using the approximate relation (17) instead of evaluating the quadratic. Equation 17 also shows clearly that the possibility of an error in the determination of L is without appreciable influence upon the values of K'_c in these experiments, since K_c^∞ is independent of L.

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[8] We are indebted to Dr. T. H Gronwall for suggesting this development.

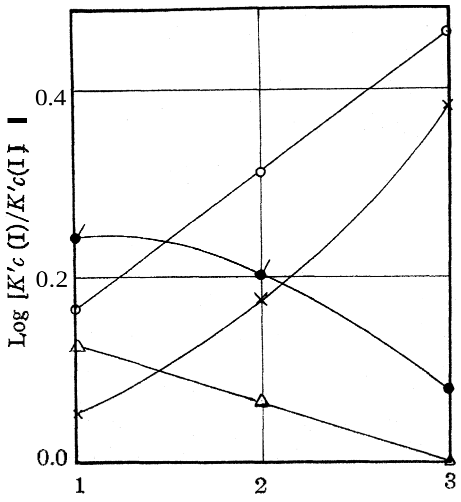
TABLE III

RATIOS OF EQUILIBRIUM CONSTANTS K'_c

Cation (M) present	MX added moles/liter	Ratios expt. no. of Table I	$\frac{K'_c(\mathrm{MCl})}{K'_c(\mathrm{MNO_3})}$	Log Col. 5
K	1.00	2/12	1.476	0.1691
K	2.00	3/13	2.057	,3132
K	3.00	11/16	2.932	,4672
Na	1.00	7/5	1.131	.0535
Na	2.00	8/10	1.513	.1798
Na	3.00	9/15	2.439	.3872
Anion (X) present			$\frac{K'_c(\mathrm{KX})}{K'_c(\mathrm{NaX})}$	
Cl	1.00	2/7	1.742	0.2411
Cl	2.00	3/8	1.594	.2025
Cl	3.00	11/9	1.201	.0795
NO_3	1.00	12/5	1.335	,1255
NO_3	2.00	13/10	1.172	.0689
NO_3	3.00	16/15	1.000	.0000
SO_4	0.50 or 1.00 *N*	6/17	1.806	,2567

V. Discussion

The most striking result of this investigation is the marked specific effect on the equilibrium constants, K'_c or K_c^∞, on changing from potassium to sodium salts and chlorides to nitrates. Thus at 4 molar potassium chloride additions, $K'_c = 96.2$, while for 4 molar sodium chloride it is 64.2.



Added salt, mole/liter.
O, KCl/KNO₃; ×, NaCl/NaNO₃; ●, KCl/NaCl; A, KNO₃/NaNO₃.

Fig. 1.

This is best shown in Table III, where we compute the ratios for K'_c (see Col. 4) at constant salt concentrations, when either the cation or anion is changed. The logarithms of these ratios are directly proportional to the change in free energy for Reaction **3** produced by changing the thermodynamic environment. These values are plotted in Pig. 1 against the molality of the added salt. It is to be noted that they are sensibly a linear function of the added salt. The theoretical significance is not entirely clear, but it is interesting to point out that in concentrated solutions the predominant specific term in Hückel's[9] equation for the variation

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[9] Hückel, *Physik. Z.*, 26, 93–147 (1925).

of the logarithm of the activity coefficient of an ion is linear in respect to concentrations.

If Bronsted's[3] theory of specific interaction were applicable at concentrations higher than 0.1 M, we should expect the equilibrium to be practically unaffected by changes in the negative ions and affected only by changes in the positive ions. However, inspection of Fig. 1 shows that the most marked change occurs when Cl is substituted for NO_3, which is not in agreement with this theory.

From the marked change in solubility which iodine exhibits on passing from a nitrate to a chloride solution, it is reasonable to suppose that this failure might be due to the variation in f_{I_2} arising from the formation of complexes of the type I_2Cl^-, as pointed out by Carter.[10]

This hypothesis can be tested by eliminating the variation in f_{I_2} through measurements on the solubility of I_2. We have accordingly computed the values of f_{I_2} in 1, 2 and 3 M potassium chloride, potassium nitrate, sodium chloride and sodium nitrate by interpolating the available data on the solubility of iodine in aqueous salt solutions.[11,12,13]

In addition we have determined the solubility of iodine in 3 M potassium nitrate and found it to be 0.00083 mole/liter at 25° when the corresponding value in pure water was 0.00134, By subtracting the values of log $[f_{I_2}$ (Solvent I)$/f_{I_2}$ (Solvent II)$]$ from the corresponding values of log $[K_f(\mathrm{I})/K_f(\mathrm{II})]$ which are equal to log $[K_c^{\infty}(\mathrm{II})/K_c^{\infty}(\mathrm{I})]$ where $K_f = \frac{f^2_{\mathrm{IV}} \times f_{I_2}}{f^2_{\mathrm{III}} \times f^2_{I^-}}$, we should eliminate most of the changes in f_{I_2} due to I_2Cl^- formation or similar mechanisms in passing from Solvent I to Solvent II, *i. e.*, we follow primarily the change in the ion activity ratio, $f^2_{\mathrm{IV}}/f^2_{\mathrm{III}} \times f^2_{I^-}$. According to the principle of specific interaction the values of log $f^2_{\mathrm{IV}}/f^2_{\mathrm{III}} \times f^2_{I^-}$ should be zero on passing from the chloride to the nitrate solvent but should possess a specific value independent of the anion on passing from potassium to sodium solvents. The result of these calculations shows that the latter conclusion is sensibly correct but the Cl^-/NO_3^- values are not zero although practically independent of concentration. The difficulty may be due in part to the fact that the iodine solubility values of different observers are not consistent. Experiments are now in progress to determine the salt effect on the I_3^- as well as I_2Cl^- equilibria to ascertain whether a better explanation can be obtained by correcting the K'_c values for the variation in $f_{I_3^-}$ and $f_{I_2Cl^-}$, before abandoning the hypothesis of specific interaction as a means of qualitatively predicting equilibria in concentrated solutions in systems of this type.

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[10] Carter, *J. Chem. Soc.*, 127, 2864 (1925); f is the stoichiometric activity coefficient.

[11] Herz and Hiebenthal, *Z. anorg. allgem. Chem.*, 177, 375 (1929), KCl and $NaCl$.

[12] Carter, Ref. 10, for $NaNO_3$.

[13] McLauchlan, *Z. physik. Chem.*, *44*, 617 (1903), for KNO_3

It is interesting to note that the experiments of Just[14] on the velocity of the forward reaction between ferricyanide and iodide ion always show a much greater velocity when the system is prepared from potassium instead of sodium salts.

TABLE IV

VELOCITY MEASUREMENTS AT 34.7°

	Init. *a*	Init. *b*	$k_{K^+} \times 10^3$	$k_{Na^+} \times 10^3$	*Added* salt
1	0.05	0.50	1.56	0.938	....
2	.0125	.50	5.64	3.07	. ..
3	.05	.375	0.699	0.510	....
4	.025	.50	2.75	1.58	....
5	.025	.50	5.61	. .	0.5 M KCl
6	.025	.50	4.55	...	0.5 M KNO_3

Table IV gives a summary of Just's measurements. k_{K^+} and k_{Na^+} are the velocity constants in the presence of K^+ or Na+ ions. It will be noted that a greater forward velocity is found for environments in which the equilibrium is displaced most to the right (larger values of K',). This holds also for additions of excess of neutral salts like potassium chloride and potassium nitrate.

From the kinetic derivation of the mass law, log K equals log $k_1 - \log k_2$, where k_1 is the velocity constant of the forward and k_2 the velocity constant of the reverse reaction. The evidence at present available indicates that the velocities of reactions between neutral molecules and ions (except for special cases like the action of Cl^- on I_2) are not subject to marked salt effects, whereas reactions between ions are subject to large effects. In the special case where k_2 is independent of the environment, then log k_1 is proportional to log K or to $-$ A F = RT ln K, the driving force of the reaction. The reaction between ferrocyanide and iodine is extremely rapid and thus far we have been unable to measure its velocity satisfactorily to ascertain the influence of salt additions on the reverse reaction.

We wish to thank Professor George Scatchard for constructive criticisms and suggestions in the revision of this paper.

Conclusions

1. The variation in the stoichiometric equilibrium constants K_c and K', for the reactions

$$2Fe(CN)_6^{---} + 21- \leftrightarrows 2Fe(CN)_6^{----} + I_2 \qquad (K_c)$$

$$2Fe(CN)_6^{---} + 3I^- \leftrightarrows 2Fe(CN)_6^{----} + I_3^- \qquad (K'_c)$$

have been studied in the presence of potassium and sodium ions as cations and also in the presence of additions of nitrates, chlorides and sulfates of potassium and sodium.

2. Marked changes in K_c and K'_c occur on changing from potassium to sodium salts, the constant being larger in the presence of potassium

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[14] Just, *Z. physik Chem.*, **63, 538 (1908).**

than for sodium salts. The free energy differences of the reaction when potassium is substituted for sodium, or chloride for nitrate, are sensibly linear functions of the concentration of added neutral salt for 1, 2 and 3 molar additions.

3. Although all the ions involved are of negative sign, the shift in equilibrium does not follow the principle of specific interaction at these high concentrations.

4. For solutions of constant thermodynamic environment, K_c^∞ (tri-iodide formation neglected) is not constant when I^- is varied, whereas K'_c (tri-iodide considered) is constant, This furnishes additional evidence for the existence of tri-iodides in solution.

5. The shift in equilibrium on changing the cation from potassium to sodium is in qualitative agreement with the measurements of the greater velocity of the forward reaction in the presence of potassium ions.

NEW YORK CITY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND]

A STUDY OF THE REACTION BETWEEN HYDROGEN SULFIDE AND SILVER

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In many of the elementary textbooks in inorganic chemistry the reaction between silver and hydrogen sulfide under normal conditions is said to give silver sulfide and hydrogen. Since the electro-potential of silver is greater than that of hydrogen, it seems rather peculiar that silver should so readily replace the hydrogen from this weak acid at ordinary temperatures. A difference in electro-potentials is, however, no criterion that the reaction would not take place, because the order of the electromotive series may be reversed in a great many different ways; but the textbooks indicate that the reaction takes place normally under room conditions.

We find several articles in the literature bearing on this subject and different views are expressed. Inasmuch as there is a difference of opinion in the literature, and many textbooks still hold to the simple replacement reaction, it was thought well to investigate the action of hydrogen sulfide on silver under room conditions, while controlling all variables as far as possible.

Historical Review

One of the earliest of the investigators to inquire into the conditions of the reaction between silver and hydrogen sulfide was J. M. Cabell,[1] who found that silver and hydrogen sulfide dried by phosphorus pentoxide

[1] Cabell, *Chem. News*, **50, 208** (1884).

did not react appreciably even after a period of four months of summer weather. F. L. Hahn[2] bubbled hydrogen sulfide through de-aerated water in which silver had been placed. He found no reaction taking place. However, on addition of some hydrogen peroxide, or on bubbling oxygen through the solution of hydrogen sulfide, the silver instantly blackened. He also could not detect any hydrogen even after boiling. He therefore expressed the opinion that oxygen enters into the reaction in the following manner

$$2Ag + H_2S + {}^1/_2O_2 \longrightarrow Ag_2S + H_2O$$

Hahn, however, quotes W. Ostwald as stating that the affinity of silver (also copper) for sulfur is so great that this metal is able to liberate hydrogen from hydrogen sulfide. J. Percy[3] is also of the opinion that the reaction is of simple replacement. Treadwell[4] on the other hand is of the same opinion as F. L. Hahn.

F. G. Keyes and W. A. Felsing[5] investigated the equilibrium existing in the reaction between silver sulfide and hydrogen at several different temperatures between 749.15–889.63°K. With the data available, they calculated the heat of reaction at those temperatures by means of the van't Hoff reaction isochore. The thermochemical equation at those temperatures was found to be

$$Ag_2S + (H_2) \rightleftharpoons 2Ag + (H_2S) + 2410 \text{ cal.}$$

thus showing that the reaction between silver and hydrogen sulfide is endothermal. This would indicate that the reaction should proceed with great difficulty at the much lower room temperature.

Experimental

Materials Used

Silver.—The silver was purified by electrolysis of the nitrate and analysis indicated that samples obtained by this method were never less than 99.84% silver.

Hydrogen Sulfide.—Hydrogen sulfide was prepared by the reaction of water on aluminum sulfide.

De-aerated Water.—De-aerated water was prepared by boiling distilled water slowly for a period of four and a half hours.

Aluminum Trioxide.—Aluminum hydroxide was precipitated from an aluminum chloride solution by the addition of ammonium hydroxide. It was then thoroughly washed free from chlorides by decantation and filtering by suction. It was then dried for two days at 80–85°. The resulting hard mass was pulverized and completely dehydrated during a period of one week at about 180°. The aluminum trioxide made in this way was found to be a very satisfactory dehydrating agent.[6]

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[2] Hahn, *Z. anorg. Chem.*, 99, 118 (1917).

[3] Percy's "Metallurgy, Silver and Gold," Part I, 1880.

[4] Treadwell, "Analytical Chemistry," Vol. I, 5th ed., p. 358.

[5] Keys and Felsing, THIS JOURNAL, 42, 246 (1920).

[6] J. W. Marden and V. Elliott, *J. Ind. Eng. Chem.*, 7, 320 (1915); F. M. G. Johnson, THIS JOURNAL, 34, 911 (1912).

Silica Gel.—A good grade of commercial gel was strongly heated for about an hour so as to be completely dry.

Analysis of Material

Silver.—The silver analysis in these experiments was carried out by dissolving the silver in nitric acid, converting it to the chloride and weighing as such.

Hydrogen Sulfide.—Hydrogen sulfide prepared by the reaction of water on aluminum sulfide was found to be completely absorbed by a 50% solution of sodium hydroxide, giving no indication of the presence of hydrogen.

Phosphorus Pentoxide as a Drying Agent.—Many investigators have used phosphorus pentoxide as a drying agent for hydrogen sulfide. The following test was run on this material and it was found unfit for use.

A stream of hydrogen sulfide was passed through a drying tube containing phosphorus pentoxide for ten minutes. The gas coming from the drying tube was led into a sodium hydroxide solution. The phosphorus pentoxide was then washed out with water and extracted with carbon disulfide. When the carbon disulfide was allowed to evaporate from an evaporating dish, yellow crystals of sulfur appeared.

The sodium hydroxide solution was treated with dilute hydrochloric acid until neutral. The sulfide ions were precipitated with an excess of cadmium nitrate. It was filtered, the filtrate being tested with sodium nitroprusside to see if all sulfide ions were precipitated out. The filtrate was found to decolorize malachite green solution (0.025 g. in 300 cc. of water), and when barium nitrate was added, a white precipitate formed. This precipitate dissolved in hydrochloric acid; the resulting solution decolorized iodine solution. These tests indicate the presence of a sulfite. Phosphorus pentoxide is therefore unfit to use as a dryer of hydrogen sulfide, as it oxidizes this gas to sulfur dioxide.

Aluminum Trioxide and Silica Gel as Drying Agents.—Two drying tubes filled with silica gel were connected to another drying tube containing aluminum trioxide. The aluminum trioxide tube was connected to a weighed phosphorus pentoxide tube; this in turn was connected to another phosphorus pentoxide tube which was connected to a suction pump. Air saturated with moisture was then drawn through the system by means of the suction pump. The weighed phosphorus pentoxide tube showed no gain in weight. This indicates the efficiency of the system. The function of the silica gel is to dehydrate the gas from most of its moisture. The aluminum trioxide removes the least traces.[6]

Analysis of the Sulfides.—The amount of combined sulfur formed was found by the increase in weight in the silver sample. As a check, the sulfide was oxidized by fuming nitric acid to the sulfate and the silver was precipitated as the chloride. It was filtered, washed, dried and weighed, to serve as a check on the silver originally used. Barium sulfate was then precipitated out from the solution. It was filtered through a weighed Gooch crucible, washed, dried and weighed. The amount of combined sulfur was calculated from the amount of barium sulfate present.

Apparatus

Reaction Chamber.—The reaction chamber consisted of an eight-ounce bottle with a two-hole stopper covering it, containing an outlet tube. Both tubes (inlet and outlet) had a piece of gray vulcanized rubber tubing fitting snugly and overlapping each end. Pieces of solid tubing which fitted snugly into the rubber tubing were placed into the overlapping parts of the rubber tubing so that the edges of each piece of solid tubing were against the ends of both the inlet and outlet tubes. Paraffin was smeared into the edges, crevices and on all the rubber tubing so that the receptacle was air-tight. A reaction chamber of this type was found to hold hydrogen satisfactorily for a period longer than that required by the experiment.

Absorption Apparatus and **Eudiometer.**—Experiment showed that with the eudiometer used as little as 0.2 cc. of hydrogen could be detected. Since in preliminary tests it was found that enough sulfide was formed for the liberation of several cc. of hydrogen, it was thought that this was accurate enough for the work.

Carbon dioxide was used in the driving out of the gases in the reaction chamber. An absorption buret was used for the absorption of carbon dioxide and hydrogen sulfide, a 50% solution of sodium hydroxide being used as the absorption medium.

The apparatus was tested by mixing a definite quantity of hydrogen with hydrogen sulfide in the reaction chamber and then analyzing the mixture. The following table gives the results of the analysis.

Amount of hydrogen originally used, cc.	4.2	3.1	6.2	2.8
Amount of hydrogen by analysis, cc.	4.0	3.0	5.9	2.7

Method of Procedure and Data

The System Air–Moisture–Hydrogen Sulfide–Silver.—Three weighing bottles with a weighed amount of silver were placed in a reaction bottle. It was closed with a rubber stopper containing an inlet and outlet tube. One of the tubes was then closed by means of a piece of solid tubing. The reaction chamber was partially exhausted, after which it was connected to a hydrogen sulfide generator until equilibrium was established between the two. The reaction chamber was clamped shut and disconnected from the hydrogen sulfide generator. The remaining end was then completely closed with another piece of sealed glass tubing. All crevices, edges, ends and rubber tubing were completely covered with paraffin. Nine such reaction chambers were prepared.

The reaction was allowed to proceed for 500 hours, after which time the contents were analyzed as described. The results found are shown in Table I. It can be seen that no hydrogen was found after the reaction had taken place.

TABLE I

REACTION OF HYDROGEN SULFIDE WITH Ag IN THE PRESENCE OF AIR AND MOISTURE AT ROOM TEMPERATURE AND PRESSURE

Silver, g.	Silver on analysis, g.	Combined sulfur		Yield of hydrogen	
		By direct wt., g	By analysis, g.	Calcd., cc.	Actual, cc.
1.0723	1.071	0.0051	0.0050	3.57	0
0.9760	0.9754	.0046	.0047	3.22	0
.8976	.8971	0032	.0032	2.24	0
.9132	.9125	.0028	.0030	1.96	0
1.0534	1.0530	.0046	.0048	3.22	0
1.2142	1.2134	.0069	.0067	4.83	0
1.0053	1.0041	.0041	.0043	2.87	0
0.9241	...	.0036	...	2.52	0
1.1723	...	.0054	...	3.78	0

The System Water–Hydrogen Sulfide–Silver (No Air).—A weighing bottle with a weighed amount of silver was placed in a reaction chamber, Water which had been boiled for four and a half hours was placed in the reaction chamber while still boiling, until the reaction chamber was nearly full. The water was boiled again for half an hour in order to rid it of any air which may have dissolved in the water during the process of transferring. The chamber was stoppered. While the water was still boiling hot, hydrogen sulfide was bubbled through the water to drive off any air which may have been present above the water. The chamber was then closed and the water allowed to cool. When cold, more hydrogen sulfide was bubbled through. The reaction chamber was then sealed up as usual. After 750 hours the hydrogen sulfide was boiled out and the silver was analyzed for sulfide. Five such reaction chambers were prepared, out of which only one showed a slight blackening of the silver. This was assumed to be an error. The results are given in Table II.

Table II

Reaction of Hydrogen Sulfide with Silver in Water Free from Air at Room Temperature and Pressure

Silver sample, g.	0.2934	0.3006	0.3249	0.2763	0.2891
Silver by anal., g.	.2929	.3002	.3249	.2754	.2884
Comb. sulfur by anal., g.	0	0	.0006	0	0
			Sl. blackening		

The System Hydrogen Sulfide–Silver–Air (No Moisture).—A weighing bottle with a weighed amount of silver which had been dried at 180° for several days was placed in a reaction chamber. The reaction chamber was then closed with a stopper containing the usual inlet and outlet tubes. One of the tubes was sealed in the usual way and the other was connected to an aluminum trioxide drying tube, which in turn was connected to two silica gel drying tubes. The reaction chamber was then partially evacuated several times, so as to make certain that the air in it was absolutely dry. The whole system was again partially evacuated and then connected to a hydrogen sulfide generator. The system was allowed to come to equilibrium with the generator and the reaction chamber was then sealed up as usual. After 600 hours the silver was weighed again and analyzed. Five such chambers were prepared, of which only one had a very slight coloration. This was assumed to be an error. The results are shown in Table III.

Table III

Reaction of Hydrogen Sulfide on Silver in the Presence of Dry Air at Room Temperature and Pressure

Silver sample, g.	0.4163	0.2993	0.3167	0.2834	0.3260
Ag after reaction, g.	.4164	.2993	.3168	.2836	.3260
Silver by analysis, g.	.4153	.2987	.3160	.2833	.3261
Comb. sulfur by anal., g.	0	0	0	.0001	0
				Sl. coloration	

The System Moisture–Air–Silver–Hydrogen Sulfide at 210°.—The open ends of four test-tubes were drawn out so as to make them easier to seal up. Silver was then placed in each test-tube. They were evacuated partially and allowed to come to equilibrium with a hydrogen sulfide generator. The tubes were then sealed off, placed in an oil-bath and heated up to 210°. They were kept at that temperature for one hour. The sealed tubes were then allowed to cool. One end of each tube was broken under a eudiometer tube containing a 50% solution of sodium hydroxide. The unabsorbed gas was tested for hydrogen and in no case was hydrogen shown to be present. The silver samples were analyzed for combined sulfur. The results are given in Table IV.

TABLE IV

REACTION OF HYDROGEN SULFIDE ON SILVER IN MOIST AIR AT 210°

Combined sulfur by analysis, g.	0.0092	0.0053	0.0051	0.0058
Calcd. yield of hydrogen, cc.	6.44	3.71	3.57	4.06
Actual yield of hydrogen, cc.	0	0	0	0

The System Hydrogen Sulfide–Silver (No Air, No Moisture).—Several test-tubes whose ends were drawn out and open were made and silver was placed in them. Dry hydrogen sulfide was then passed through to drive out the air. The tubes were sealed off at both ends and heated in an oil-bath for an hour and a half at 190°. The tubes were cooled. One end of each tube was broken under a eudiometer tube containing a 50% solution of sodium hydroxide. The tubes were found to contain 2.1 cc. and 1.3 cc. of hydrogen. No attempt was made to obtain an equilibrium reaction.

A test-tube containing silver and sulfur was sealed up and kept at room temperature. In one day the silver was found to have blackened. In a week's time practically all of the silver was converted to the sulfide.

Discussion of Results

The results of J. M. Cabell and F. L. Hahn have been fully confirmed in the present investigation. Furthermore, it has been shown conclusively that no hydrogen is formed under conditions where both moisture and air are present. The one experiment in which hydrogen was formed is what one would expect from the thermochemical equation $2Ag + H_2S + A \longrightarrow Ag_2S + H_2$, the reaction being endothermal in nature.

The results of this investigation would indicate almost conclusively that oxygen plays a part in the reaction, either in atomic, molecular or combined form.

F. G. Donnan and T. W. A. Shaw[7] have demonstrated that the oxygen dissolved in molten silver exists as atomic oxygen dissolved in a purely physical way, or it exists as ionic oxygen in the form of silver oxide.

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[7] Donnan and Shaw, J. *Soc. Chem. Ind.*, 29,987 (1917)

B. Brauner[8] has demonstrated that 152.2133 g. of silver gave off 0.844 cc. of oxygen between 450° and red heat. J. Percy[3] states that when silver is melted in the air some of it is oxidized to silver oxide. This substance on cooling tends to separate out from the silver since it is only sparingly soluble in solid silver. On further cooling the silver oxide breaks up into silver and gaseous oxygen. However, it is conceivable that a trace of silver oxide remains in solution in the solid silver. It is also reasonable to suppose that some silver oxide is left at the lower temperatures, since the decomposition of silver oxide is an equilibrium reaction. J. Percy also states that silver retains 0.545 of its volume of oxygen when cold.

I. Langmuir[9] has demonstrated that oxygen is adsorbed onto the surfaces of many metals in the form of stable films of atoms. These oxygen atoms are attached to the metallic atoms by primary valences. He has also shown that hydrogen molecules are adsorbed by platinum, tungsten and probably by other metallic surfaces in the form of atoms. The hydrogen so adsorbed by the metal is therefore able to react with the oxygen ions, if an oxide is present, or with the oxygen atoms if oxygen is adsorbed as atoms.

With the above facts in mind, one might formulate several theories to account for the reaction between silver and hydrogen sulfide. The following explanation seems quite feasible.

Hydrogen sulfide in contact with a limited supply of oxygen tends to be oxidized to water and sulfur: $H_2S + {}^1/_2O_2 \longrightarrow H_2O + S$, this occurring usually in solution. It is therefore conceivable that hydrogen sulfide gas in the presence of moisture may be oxidized by contact with the oxygen atoms or molecules attached to the silver surface, to water and sulfur. The sulfur atoms thus formed combine instantaneously with the silver atoms to form the sulfide.

Since the supply of oxygen atoms, molecules or ions on the silver surface is very small, it is evident that air or any other easily accessible source of oxygen must be in contact with the silver for the reaction to proceed to any extent. F. L. Hahn[2] reports that polysulfides react with silver to form the sulfide without the presence of oxygen. The reaction here as in the case of monosulfides is probably not that of a simple replacement, but is more likely to be due to the loose linkage of a sulfur-to-sulfur bond, which in contact with silver is easily broken with the consequent formation of the sulfide of silver.

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Conclusions

1. Hydrogen is not formed as the result of the reaction between hydrogen sulfide and silver in the presence of air and moisture.

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[8] Brauner, J. *Chem. Soc.*, 55,400 (1889).

[9] Langmuir, *Trans. Faraday Soc.*, **17,607 (1922).**

2. The results of J. M. Cabell and F. L. Hahn have been fully confirmed: the presence of both oxygen and moisture is required for the reaction between hydrogen sulfide and silver to take place at ordinary temperatures and pressures.

3. A theory has been advanced which takes into consideration the need for both oxygen and moisture.

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

HYDROGENATION OVER METALLIC CESIUM

BY DOUGLAS G. HILL AND GEORGE B. KISTIAKOWSKY

RECEIVED AUGUST 16, 1929 PUBLISHED MARCH 6, 1930

If hydrogenations can be induced by alkali metals as catalysts, one would look to the intermediate compound theory for explanation, as the hydrides of these metals are readily formed and decomposed at moderate temperatures. Experiments on one such reaction over metallic cesium seem to indicate, however, that although hydrogenation occurs the hydride is not the catalyst and even hinders the reaction.

Experiment showed that ethylene and hydrogen reacted when admitted to distilled cesium even at room temperature. The rate as measured by pressure drop gave evidence of poisoning of the catalyst, for the decrease upward of ten millimeters per hour at the start, diminished steadily, and the total pressure only approached that consistent with ethane formation after a long period of time. At 200° the process was much more rapid, but a similar diminution in rate was observed.

Reaction was also found between carbon monoxide and hydrogen, commencing very rapidly at room temperature, and as rapidly diminishing, becoming zero at a pressure not susceptible of ready interpretation. Thus poisoning was again evident, though the experimental difficulties in analyzing the gases were such that the quantitative measurements were performed on the more easily handled ethylene and hydrogen.

Analysis showed that the reaction produced ethane, and also that (unaccounted for) hydrogen had disappeared from the gas phase. This is ascribed to the formation of cesium hydride, for the once silvery metal was covered with a white layer. Confirmation of this hypothesis was sought by heating the pure metal in an atmosphere of hydrogen, in which case the pressure decreased, and a similar white coating was obtained. When ethylene was admitted to this supposed hydride at room temperature no pressure change was observed, but analysis of the gas after some hours showed the presence of small quantities of ethane. Moissan[1] failed to find any reaction between ethylene and cesium hydride, a discrepancy

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[1] Moissan, *Bull. soc. chim.*, **31**, **556** (1904), *et al.*

to be explained by the slowness of the reaction, rendering his flow method too insensitive. At 200° the reaction was quite rapid, and a slight pressure decrease was observed. The hydrogen was almost completely removed from the hydride, for the white substance disappeared and the surface, although dull, was once more metallic in appearance. Ethane and some hydrogen were found in the gas, the latter arising from the thermal decomposition of the hydride, which is appreciable at that temperature' though extremely small at 25°. The pressure decrease may be due to adsorption of ethylene on the metal surface, or to a polymerization catalyzed by the metal. Both processes are believed to occur.

The catalytic activity depended on the treatment of the metal. When the surface had been heavily coated with hydride by prolonged heating in hydrogen, its effect on an ethylene hydrogen mixture at room temperature was very slight.

When the hydride was removed as above by heating with ethylene, the activity was much enhanced. Analysis of an ethylene–hydrogen mixture after a considerable pressure drop had occurred showed the presence of large amounts of ethane, more indeed than corresponded to the ethylene introduced. This phenomenon, which appears to be real, must be due to ethylene adsorbed during the dehydrogenation process. Excess hydrogen disappeared in the reaction, and the white coat attributed to hydride was again formed.

If, after removal of the hydride as above, the bulb was heated in vacuum so that a fresh surface of pure cesium was distilled to the cooler parts of the bulb, the reaction rate was the greatest of all. The reaction products were ethane and hydride as before.

An attempt was made to cause nitrogen and hydrogen to react in the same way. There was a pressure decrease, but analysis showed that it was due to the formation of hydride, with perhaps a small amount of nitride. Ammonia was not found, nor was the amide which Moissan obtained from nitrogen and cesium hydride, this latter presumably because the total quantity of hydride was so small in these experiments.

An attempt to repeat the ethylene–hydrogen reaction over sodium gave nothing but hydride formation until a temperature close to 300° was reached, when the ethylene began to polymerize rapidly and to cover the surface with tar. A small amount of ethane was formed at this temperature, however, before the tar had rendered the surface completely inactive.

These results would seem to show that even over an alkali metal only adsorbed hydrogen is available for hydrogenation, and that hydride formation serves merely to diminish the free surface. Even over a surface as completely covered with hydride as possible, however, some reaction is observed, for the equilibrium pressure of hydrogen over so unstable a compound must be high enough at all temperatures so that some free surface is present. When part of the surface is covered with adsorbed ethylene, reaction is hindered, as the hypothesis would demand.

That these reaction conditions have some generality is shown by the work of Pease and Stewart,[2] who investigated the same reaction over calcium hydride and metallic calcium. The hydrogenation of ethylene over calcium does not go through the hydride stage, although this substance is an effective catalyst for the reaction.

One may not venture, however, to extend these principles, for Weichselfelder and Kossodo[3] have shown that in some cases of hydrogenation over nickel, and over nickel hydride, formation and decomposition of the hydride undoubtedly took place. It thus is impossible to predict the mechanism of such catalyzed reactions until further experimentation has furnished a clue.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 233]

THE USE OF THE IODINE MONOCHLORIDE END-POINT IN VOLUMETRIC ANALYSIS. I. THE TITRATION OF IODIDE

BY ERNEST H. SWIFT

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Introduction

In the so-called "iodate methods"[1,2] of volumetric analysis there is usually added to a hydrochloric acid solution of the reducing substance to be analyzed a standard solution of an iodate until the iodine at first liberated is oxidized to iodine monochloride by the reaction $I_2 + 2HCl + O$ (from iodate) $= 2ICl + H_2O$. The end-point is determined by the disappearance of the iodine color in an immiscible organic solvent, usually carbon tetrachloride or chloroform, which is shaken in a closed flask with the aqueous solution. This end-point is sharp and permanent, and permits of back titration. According to Kolthoff[3] the sensitivity of the detection of free iodine by this method exceeds that by the conventional starch indicator, and a correction factor for the end-point is unnecessary. Results given below of tests which have been made under various conditions confirm this and show the extreme sensitivity of the end-points obtained.

[2] Pease and Stewart, THIS JOURNAL, 47, 2763 (1925).

[3] Weichselfelder and Kossodo, Ber., 62B, 769 (1929).

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[1] Andrews, Z. anorg. *Chem.*, 36, 83 (1903); THIS JOURNAL, 25, 756 (1903).

[2] Jamieson, "Volumetric Iodate Methods," The Chemical Catalog Co., New York, 1926.

[3] Kolthoff and Furman, "Volumetric Analysis," John Wiley and Sons, New York, 1929, Vol. II, p. 352.

Adequate use does not seem to have been made of the fact that, by the addition of a small quantity of iodine monochloride to a hydrochloric acid solution of the substance to be titrated, this end-point, which depends only upon the oxidation of the iodine to iodine monochloride, can be used not only with iodate, but with any other standard oxidizing solution which rapidly and completely causes the formation of the monochloride. Iodide has, to be sure, been titrated with permanganate to iodine monochloride by McCulloch[4] and by Willard and Fenwick,[5] the latter having determined the end-point electrometrically. Willard and Young[6] have also titrated iodide to iodine monochloride with a ceric sulfate solution, but have determined the end-point electrometrically.

To ascertain what standard oxidizing agents could be used with the iodine monochloride end-point, there have been made a study and comparison of the titration of iodide with standard solutions of potassium iodate, potassium permanganate, ceric sulfate and potassium dichromate. These results, presented in this paper, show the conditions, especially as regards the concentration of hydrochloric acid, under which accurate titrations can be made with all of these solutions using the iodine monochloride end-point. It would thus seem possible under the proper conditions to substitute permanganate and ceric solutions, or dichromate if desired, for iodate in the titration of the numerous substances for which methods have been developed by the use of a standard iodate solution. Several advantages would be gained. Thus certain substances, notably arsenic and antimony, which are not readily titrated with permanganate or ceric solutions without the aid of catalytic agents, may be readily titrated with these solutions under the conditions of the iodine monochloride end-point; and the necessity of using electrometric end-points with ceric solutions is avoided. Moreover, the danger of loss of iodine, which is inherent when iodate is used and considerable amounts of iodine are liberated during the titration, is eliminated when only a small amount of iodine monochloride is added and another oxidizing agent substituted for the iodate. Finally, the possibility of standardizing several oxidizing solutions against the same primary standard under very similar conditions is gained. Thus there are presented in the following paper the results of a study of the standardization of solutions of permanganate and of ceric sulfate against arsenious oxide.

The disadvantages of this method of determining the end-point are the necessity for vigorous shaking of the solution in flasks with ground-glass stoppers and the rather large quantities of hydrochloric acid required. The first is minimized by the fact that one accustomed to the

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[4] McCulloch, *Chem. News,* 57, 135 (1888).

Willard and Fenwick, THIS JOURNAL, 45, 624 (1923).

[6] Willard and Young, *ibid.,* 50, 1368 (1928).

method can approximate the position of the end-point both by the change in the color of the aqueous layer and by the intensity of the iodine color in the organic solvent, and by the fact that a back titration is readily made. It has also been found that the concentration of hydrochloric acid, 3.5–4 molal, thought to be the minimum[7] for obtaining this end-point can be somewhat reduced in certain titrations.

Experimental Methods and Results

Substances and Solutions.—The potassium iodide used was of "analytical chemical" grade and was proved to be free from iodate and from an appreciable quantity of alkali. The calculated weight of the dried salt was dissolved and diluted to the proper volume to make the resulting solution 0.04 molal.

The potassium iodate was of the same grade and was proved to be free from iodide. The solution was prepared as above to be 0.025 molal.

The potassium permanganate solution was standardized against sodium oxalate obtained from the Bureau of Standards.

The ceric sulfate solution was supplied through the courtesy of Dr. A. H. Kunz of this Laboratory. It had been prepared by ignition of C. P. ceric oxalate to oxide and dissolving the oxide in sulfuric acid. It was 0.05950 molal in ceric salt and 0.5 molal in sulfuric acid. It had been standardized against Bureau of Standards sodium oxalate under the conditions recommended by Willard and Young,[8] the end-point being determined electrometrically.

The potassium dichromate solution was prepared by weighing the proper amount of the "analytical chemical" grade of material, dissolving it and diluting the solution to make it 0.1 N.

Sensitivity of the Detection of Iodine by Carbon Tetrachloride.—To 50 ml. of 1 molal hydrochloric acid were added 0.1 ml. of 0.04 molal potassium iodide and 5 ml. of carbon tetrachloride and the solution was then titrated with 0.00025 molal potassium iodate. Upon adding 0.12 ml. a barely perceptible color was observed, most apparent against a white background. With 0.16 ml. the color was very definite and with 0.24 ml. it was obvious. The total amount of iodine present when its detection was definite was approximately 0.03 mg., its concentration being 2.4×10^{-6} molal. It should be noted that this test, unlike the starch test, is made somewhat less sensitive by the presence of large amounts of iodide; also that when the titration is made with iodate

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[7] Andrews (Ref. 1) states, apparently as the result of experiments in which iodide was titrated with "chlorine water" and successively larger volumes were found to be required as the acid concentration was reduced below 5.5 molal, that a high concentration of hydrochloric acid is necessary because of the hydrolysis of the iodine monochloride according to the equation $ICl + H_2O = IOH + HCl$, and "the iodous hydroxide ('hypoiodous acid'), which is formed, undergoing spontaneous conversion into iodic acid, etc." Since this decomposition would seem to result in the formation of iodine and some higher valence form of iodine, since the constant K for $(I_2)(ICl_3) = K(ICl)^3$ has been found to be at 1.1×10^{-11} and practically independent of the acid concentration down to 4 molal hydrochloric acid [Forbes, Glass and Fuoss, THIS JOURNAL, 47, 2892 (1925)], and since it was found that iodine monochloride solutions could be largely diluted without appreciable formation of iodine, it appeared that the effect might be one of rate rather than one of hydrolysis. Experiments, the results of which are shown, seem to confirm this belief.

[8] Willard and Young, *ibid.*, 50, 1332 (1928).

and large quantities of iodine monochloride are present, the yellow color of the iodine monochloride makes the test somewhat less sensitive. Even so, 50 ml. of a solution which was approximately 0.02 molal in ICl and 6 molal in hydrochloric acid could be consistently titrated back and forth with 0.06–0.08 ml. of solutions of potassium iodide and iodate which were 0.004 and 0.0025 molal, respectively.

Titration of Iodide with Iodate.—To afford a check on the concentration of the potassium iodide solution and to study the effect of the concentration of the hydrochloric acid present it was titrated with the standard iodate solution.

The procedure was to pipet the iodide solution into a 250-ml. conical flask provided with a ground-glass stopper, and then to add 5 ml. of carbon tetrachloride and the hydrochloric acid. The flask was cooled with tap water and the carbon tetrachloride examined just before beginning the titration to be sure that it was colorless. The iodate was usually run in rapidly until within approximately 1 ml. of the end-point. After shaking the solution, the flask was cooled with tap water and a small amount of water poured around the stopper before opening it, so that as the stopper was withdrawn any iodine vapor or solution around it would be drawn into the flask and not expelled. The amounts of the reagents used and the results are shown in Table I.

TABLE I

TITRATION OF IODIDE WITH IODATE

Expt.	KI, ml.	12 *M* HCl, ml.	KIO_3, ml.	HCl, final molality	KI, molality found
1	25	25	20.02	4.3	0.04004
2	25	25	20.01	4.3	.04002
3	50	50	40.00	4.3	.04000
4	50	50	39.99	4.3	.03999
5	25	20	20.00	3.5	.04000[a]
6	25	10	20.01	2.1	.04002[b]
7	25	20[c]	20.01	1.8	.04002[b]
8	50	20[c]	40.04[d]	1.0	.04004[b]
9	25	20[c]	20.01	1.8	.04002[b]

[a] After reaching the end-point 65 cc. of water was added. No return of iodine color. One drop of 0.04 *M* KI restored the color. [b] End-point slow. [c] Six *M* HCl used. [d] 39.93 ml. of KIO_3 was added and the solution allowed to stand for two hours before finishing the titration.

The results of Expts. 5–8 in the above table seem to show that the necessity for a high acid concentration is not due to hydrolysis of the iodine monochloride, but to a slow rate of reaction as the end-point is approached. To further confirm this, after completing the titration of Expt. 8, an excess of 0.10 ml. of potassium iodate was added and the solution allowed to stand for an hour; then upon titrating with iodide the first drop, 0.03 ml., caused an iodine color which faded only after shaking for five to ten minutes. This was repeated until 0.03 ml. excess of iodide had been added, after which the color remained permanent. In another experiment 10 ml. of a solution approximately 0.02 molal in iodine monochloride and 6 molal in hydrochloric acid was pipetted into a flask and 5 ml. of carbon tetrachloride and 90 ml. of water were added. The faint color of the iodine in the carbon tetrachloride seemingly increased very slightly. Another 100 ml. of water was added with no appreciable change in the color even on standing for one hour. Upon adding 0.1 cc. of 0.025 molal iodate this color slowly but completely disappeared. In another experiment 10 ml. of the same stock solution of iodine monochloride was very carefully titrated with iodate solution until the carbon tetrachloride solution showed no perceptible iodine color. To it was added 190 ml. of water and the solution was allowed to stand for an hour. No iodine color developed in the carbon tetrachloride. It then required only one drop of 0.04 molal potassium iodide solution to produce an immediate and permanent color.

In Expt. 9 the total amount of iodate was added and the solution then shaken intermittently until the end-point was attained; this required four and one-half minutes. The solution was then let stand for ten minutes, after which 0.03 ml. of 0.05 molal potassium iodide was added; a permanent color was produced in the carbon tetrachloride. It should be noted that during the four and one-half minutes it was evident after each period of shaking, usually ten to fifteen seconds, that the iodine color was decreasing, so that the probability of overrunning the end-point can be minimized. Likewise, the solution can be back titrated with iodide solution to a permanent color. It is thus possible under certain conditions to titrate successfully iodide with iodate in 2 molal hydrochloric acid; however, where a quick end-point is desired, a higher concentration is advisable. Below 2 molal acid the rate of the reaction is too slow to be of practical use.

Titration of Iodide with Permanganate.—Table II shows the results obtained upon titrating iodide with standard permanganate solution. The procedure was essentially the same as in the iodate titrations. It should

TABLE II

TITRATION OF IODIDE WITH PERMANGANATE

Expt.	KI, ml.	$KMnO_4$, ml.	HCl, final molality	KI, molality found
1	25	20.18	4.2	0.04008
2	50	40.34	4.2	.04006
3	25	20.16	4.2	.04004
4	25	20.16	4.2	.04004
6	25	20.32	1.1	,04035[a]
6	25	20.15	1.8	.04002[b]
7	25	20.15	3.0	,04002
8	50	40.30	3.3	,04002
9	25	20.18	6.3	.04008

[a] End-point very slow. [b] $KMnO_4$ added all at once; required five minutes for appearance of end-point.

be noted that, even upon adding a slight excess, the usual color of the permanganate is not obtained in the solution, but the excess is reduced, the iodine monochloride probably being oxidized to trichloride.

The characteristics of the titration with permanganate were very similar to those with iodate. The rate at which the end-point was attained with the same acid concentration was perhaps slightly slower with the permanganate. This was contrary to what had been expected. It appears that about 0.1% too much permanganate is required. This may be due to slightly overrunning the end-point or some irregularity in the reaction. The magnitude of the effect is too close to the possible experimental error to draw definite conclusions.

Titration of Iodide with Ceric Sulfate.—Table III shows the results obtained upon titrating iodide with ceric sulfate solution by the same procedure.

TABLE III

TITRATION OF IODIDE WITH CERIC SULFATE

Expt	KI, ml. taken	$Ce(SO_4)_2$, ml. used	HCl, final molality	KI, molality found
1	20	26.90	6	0.04001
2	10	13.43	6.5	.03995
3	10	13.41	6.5	.03989
4	10	13.42	5.5	.03992
5	10	13.43	5.5	.03995
6	25	33.53	3.6	.03990
7	25	33.59	3.6	.03997
8	10	13.43	5.5	.03995
9	10	13.44	4.8	.03998
10	10	13.43	4.0	.03995
11	10	13.43	3.5	.03995[a]
12	10	...	3.0	......[b]

[a] End-point slow. [b] No end-point even after fifteen minutes.

When titrating iodide with ceric sulfate in 3 molal hydrochloric acid the iodine monochloride end-point is so slow as to be impracticable; with 3.5 molal acid care has to be taken not to overrun the end-point. These results are in approximate agreement with those of Willard and Young[6] using an electrometric end-point. The slightly low molality of the potassium iodide may be due to a loss of iodine, as reported by these authors, although this effect has not been apparent in the iodate and permanganate titrations and is much smaller than the effect noted by them. Special precautions, such as cooling the solutions, the use of glass-stoppered flasks with small mouths, and not shaking or stirring the solution except when the flask was closed, were taken to avoid serious error from this source.

Titration of Iodide with Potassium Dichromate.—The same procedure was used in these titrations as in those with the other oxidizing solutions. The results are shown in Table IV.

TABLE IV

TITRATION OF IODIDE WITH POTASSIUM DICHROMATE

Expt.	KI, ml. taken	$K_2Cr_2O_7$, ml. used	HCl, final molality	KI, molality found
1	25	20.04	7.5	0.04008[a]
2	25	20.02	8.5	.04004
3	25	19.99	7.5	.03998[b]
4	10	8.01	8.8	.04005

[a] End-point very slow. [b] End-point overrun, back titrated with iodide.

In other experiments not shown in the table satisfactory end-points were not obtained until the solution was approximately 8 molal in hydrochloric acid.

Summary

The advantages have been pointed out of using the iodine monochloride end-point in the titration of reducing substances with standard oxidizing solutions. This process depends upon the oxidation of iodine in a hydrochloric acid solution to iodine monochloride by the reaction $I_2 + 2HCl + O = 2ICl + H_2O$, the disappearance of the iodine color being determined by shaking with an immiscible solvent.

The use of iodine monochloride as an indicator with standard oxidizing solutions other than iodate is suggested. This substitution avoids the liberation of large amounts of iodine in the solution being titrated; for then the addition of only sufficient iodine monochloride to serve as an indicator is necessary. No correction factor is necessary either for the iodine monochloride added or the sensitivity of the end-point.

Experiments have determined the conditions under which iodide can be accurately titrated to iodine monochloride with iodate, permanganate, dichromate and ceric salt solutions. The titration with dichromate requires a solution approximately 8 molal or more in hydrochloric acid.

The results indicate that a high concentration of acid is necessary in titration of this type mainly because of the slow rate at which iodine is oxidized to iodine monochloride.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 234]

THE USE OF THE IODINE MONOCHLORIDE END-POINT IN VOLUMETRIC ANALYSIS. II. THE TITRATION OF ARSENIOUS ACID WITH PERMANGANATE AND WITH CERIC SULFATE

BY ERNEST H. SWIFT AND CARTER H. GREGORY

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Introduction

The advantages of the use of the iodine monochloride end-point and of its use with standard oxidizing solutions other than iodate have been discussed in the preceding paper. The titration of arsenious acid with permanganate solutions has presented a troublesome problem, of which the literature is too voluminous to be discussed in detail here.[1] Briefly, it may be stated that in sulfuric acid solution the rate of the reaction as the end-point is approached becomes very slow and various colored compounds form to such an extent that the titration is not recommended, even at 100°. In a hydrochloric acid solution at room temperature the same difficulties are encountered, but the titration may be made if the solution is heated to boiling. It has also been found by several workers[2] that small amounts of iodine or bromine compounds catalyze the reaction.

In view of the fact that arsenious acid can be titrated rapidly and accurately at room temperature with standard iodate solution using the iodine monochloride end-point, and in view of the just mentioned catalysis by iodine compounds, it seemed quite probable that permanganate could be substituted for iodate if a little iodine monochloride were added to serve as an indicator. This was found to be the case. The results of a study of this titration and of the standardization of a permanganate solution against arsenious oxide are shown below.

The successive reactions involved in the process may be represented as follows

$$\begin{aligned} &H_3AsO_3 + 2ICl + H_2O = H_3AsO_4 + I_2 + 2HCl \\ &H_3AsO_3 + O \text{ (from } KMnO_4) = H_3AsO_4 \\ &I_2 + 2HCl + O \text{ (from } KMnO_4) = 2ICl + H_2O \end{aligned}$$

The titration of arsenious acid with ceric sulfate solution has been studied by Willard and Young.[3] They found the reaction in a hydrochloric acid solution to be too slow for use at room temperature, but to be

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[1] For reviews of this subject see Hall and Carlson, THIS JOURNAL, 45, 1615 (1923), or Kolthoff and Furman, "Volumetric Analysis," John Wiley and Sons, Inc., New York, 1929, pp. 2, 285, 304.

[2] (a) C. Lang, *Chem.-Ztg.*, 37, 774 (1898); *Chem.-Ztg. Rep.*, p. 48 (1905); (b) R. Lang, Z. *anorg. allgem. Chem.*, 152, 203 (1926); (c) O. Cantoni, *Ann. chim. appl.*, *16*, 153 (1926); (d) Pročke and Svéda, *Chem. Zentr.*, I, 1859 (1926).

[3] Willard and Young, THIS JOURNAL, 50, 1372 (1928).

sufficiently rapid if the temperature were above 70° and if 15 ml. of concentrated hydrochloric acid per 100 ml. of solution were present. They also found that this reaction was catalyzed by bromine or iodine compounds and adopted the use of iodine monochloride since it theoretically would require no correction factor when used in a hydrochloric acid solution. Titrations could be made at room temperature. They then studied the standardization of ceric sulfate solutions against arsenious oxide; and while very reproducible results were obtained, they were consistently about 0.3% lower than the normality for the ceric sulfate solution found by standardization against electrolytic iron and sodium oxalate. They consequently recommend a correction factor of 1.003 for the titration. End-points were determined electrometrically.

The experiments to be described here show that the iodine monochloride end-point can be used in titrating arsenite with ceric sulfate, and that a correction factor is not necessary in the standardization of ceric sulfate against arsenious oxide, either in using the iodine monochloride or the electrometric end-point, if a sufficiently high concentration of hydrochloric acid is maintained in the solution.

We wish to thank Dr. A. H. Kunz for his generous assistance and for the use of the apparatus with which the electrometric titrations were made.

Experimental Methods and Results

Substances and Solutions.—The potassium permanganate solution was standardized against sodium oxalate obtained from the Bureau of Standards. Weight burets were used. The values obtained were 0.09930 and 0.09921 equivalents per 1000 grams of solution.

The ceric sulfate solutions were prepared by treating technical CeO_2 with concentrated sulfuric acid and then diluting the mixture to the desired volume. A small insoluble residue was removed by filtration through asbestos. The solutions were approximately 0.5 molal in sulfuric acid.

The arsenious acid used was of "analytical chemical" grade, accompanied by an analysis of the other constituents present. It was dried over sulfuric acid, the proper amount weighed out, dissolved in sodium hydroxide, the solution nearly neutralized with hydrochloric acid and then diluted to volume. The weight of the solution was also taken.

The iodine monochloride solution was prepared by adding to 20 ml. of 0.025 molal potassium iodate 25 ml. of 0.04 molal potassium iodide and 40 ml. of 12 molal hydrochloric acid. A few ml. of carbon tetrachloride was then added and the solution titrated with iodate or iodide until a barely perceptible iodine color remained in the carbon tetrachloride. The solution was thus approximately 0.017 molal in iodine monochloride and 5.5 molal in hydrochloric acid.

Titration of Arsenious Acid with **Permanganate.**—The procedure used was to pipet the arsenite solution into a 250 ml. conical flask fitted with a ground-glass stopper (if weight burets were used this solution was then weighed), and then to add the volume of 12 molal hydrochloric acid necessary to give the desired acid concentration at the end-point. There were then added 3-4 ml. of carbon tetrachloride and 5 ml. of 0.017 molal iodine monochloride solution and the solutions titrated with permanganate until the iodine color in the carbon tetrachloride disappeared. Vigorous shaking of the solution is necessary as the end-point is approached in order to be sure that an equilibrium is attained between the carbon tetrachloride arid aqueous layer. In Table I are shown the results of titrations as the hydrochloric acid concentration was varied. In each case 25 ml. of the arsenite solution was taken. The volume of permanganate calculated to be required was 20.14 ml.

TABLE I

TITRATION OF ARSENITE WITH PERMANGANATE

Expt.	HCl (sp. gr 1 18) added, ml	Final molal concn. of HCl	$KMnO_4$ used, ml.
1	4.5	1	20.27[a]
2	10	2	20.13
3	16.7	3	20.15
4	25	4	20.14

[a] End-point very slow.

It is thus seen that it is possible to titrate arsenious acid by this method in as low as 1 molal hydrochloric acid, although at this concentration the solutions have to be shaken for two to four minutes after each addition of permanganate. In view of the tendency of one not familiar with the method to over-run the end-point, a higher concentration of acid is advisable for accurate work. At no time during the titration were there any colored compounds formed in the solution even though most of the permanganate was run in very rapidly.

Using weight burets and a solution 4 molal in hydrochloric, acid the permanganate solution was standardized against the solution of the arsenious acid with the results shown in Table II.

TABLE II

STANDARDIZATION OF PERMANGANATE AGAINST ARSENIOUS OXIDE

Expt.	As_2O_3 soln., g.	$KMnO_4$ soln., g.	Normality $KMnO_4$ equiv./1000 g.
1	25.06	20.15	0.09922
2	25.08	20.18	.09915
3	25.10	20.16	.09933
4	25.10	20.15	.09938
6	25.11	20.18	,09927
		Average	.09927

It is very probable that the somewhat lower values for the first two results are due to slightly over sunning the end-point, as this was more carefully guarded against in the subsequent titrations. It is thought that these results are in such close agreement with the value, 0.09930 equivalent per 1000 g., obtained by the sodium oxalate method, as to warrant recommending this method for the standardization of permaaganate solutions against arsenious oxide.

Standardization of the Ceric **Sulfate Solutions** against Sodium **Oxalate.**—The desired amount of sodium oxalate was weighed, dissolved and diluted in a volumetric flask. Aliquot portions were then taken out with a 50-ml. pipet. The flask had been calibrated against this pipet. The titration was carried out under the conditions recommended by Willard and Young,[4] the solution being kept above 70° and 5 ml. of sulfuric acid (sp. gr. 1.83) being used. The end-points were determined by several methods. The first detectable yellow color given by an excess of the ceric solution was noted and this estimated by matching the color in another beaker containing the same volume of acid and water. The excess was also determined by cooling the solution under carbon dioxide, adding potassium iodide and then titrating the iodine liberated with 0.01 normal thiosulfate. The end-points were found to be unstable if this titration was made without excluding the air. Finally, the end-point was determined electrometrically. The excess required in visually determining the end-point was approximately 0.1 ml. of a 0.04 molal ceric solution. The values obtained by the various methods agreed to 0.01 ml. The values obtained for the concentration of the ceric sulfate solution are shown in Table III. The weight of sodium oxalate taken was in each case 0.093269 g. A weight buret was used for the ceric sulfate.

TABLE III

STANDARDIZATION OF CERIC SULFATE AGAINST SODIUM OXALATE

Number	$Ce(SO_4)_2$ used, g.	$Ce(SO_4)_2$ per 1000 g., mole
1	37.47"	0.03715
2	$37.48^{a,b}$	.03714
3	37.47^{b}	.03715
4	37.48^{c}	.03714
	Average	.03714

End-point noted visually, corrected by blank. [b] End-point noted visually, corrected iodometrically. [c] End-point determined electrometrically, also iodometrically.

Titration of Arsenious Acid with Ceric **Sulfate.**—The experiments given in Table IV show the effect of the hydrochloric acid concentration on the titration. The procedure was the same as that used in titrating arsenious acid with permanganate. The volume of arsenious acid taken was in every case 10 ml., then sufficient 12 molal hydrochloric acid was added to make the final concentration that shown. Five ml. of iodine

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[4] Willard and Young, THIS JOURNAL, 50, 1322 (1928).

monochloride solution was used. The volume of ceric sulfate calculated to be required was 20.57 ml.

TABLE IV

EFFECT OF HYDROCHLORIC ACID ON THE TITRATION OF ARSENIOUS ACID WITH CERIC SULFATE

Final concn of HCl, *M*	$Ce(SO_4)_2$ used, ml.	Character of end-point
2	20.61	Very slow, impractical
3	20.54	Slow
4	20.54	Rapid
4	20.55	Rapid
4	20.55	Rapid
4	20.55	Rapid

It is seen that the necessary concentration of hydrochloric acid is higher than that for the permanganate titration, and that it corresponds to that required in the titration of iodine with ceric sulfate.

By standardizing the ceric sulfate solution against arsenious acid, maintaining the hydrochloric acid at 4 molal and using weight burets, the results shown in Table V were obtained.

TABLE V

STANDARDIZATION OF CERIC SULFATE AGAINST ARSENIOUS ACID

Arsenious acid, g. of soln.	Ceric sulfate, g. of soln.	Concn. of $Ce(SO_4)_2$ mole per 1000 g.
20.005	42.94	0.03717
19.986	42.90	.03717
19.985	42.92	.03715
	Average	.03716

This value agrees to better than 0.1% with the value given by the sodium oxalate standardization and indicates that ceric sulfate solutions can be standardized very accurately against arsenious acid. It is to be noted that the deviation is in the opposite direction from that observed by Willard and Young.[3] In their standardization the concentration of the hydrochloric acid at the end-point was less than 2 molal. In view of the slow rate at which an equilibrium was established in our experiments at 2 molal acid, it seemed probable that their deviation might be caused by a similar effect. Accordingly, a different ceric sulfate solution was standardized against sodium oxalate, the end-points being determined electrometrically, and its normality found to be 0.05658. It was then titrated against the arsenious acid solution, using the iodine monochloride end-point. Finally, duplicating closely the conditions of Willard and Young, the end-point was determined electrometrically with the final acid concentration 4 and 1.8 molal. The results are shown in Table VI. In all cases 20 ml. of arsenite was taken. In Expts. 1–2, 5 ml. was used, but in Expts. **3–7** only 2 ml. of the iodine monochloride solution.

TABLE VI

TITRATION OF CERIC SULFATE AGAINST ARSENIOUS ACID UNDER VARIOUS CONDITIONS

Expt.	Final vol., ml.	Final concn., HCl M	Method of detg. end-point	$Ce(SO_4)_2$ used, ml	$Ce(SO_4)_2$, M
1	75	4	Iodine	28.24	0.05659
2	75	4	Iodine	28.26	.05655
3	130	4	Electrometric	28.24	.05659
4	130	4	Electrometric	28.23	.05661
5	130	1.8	Electrometric	28.28	.05642
6	130	1.8	Electrometric	28.35	.05630
7	130	1.8	Electrometric	28.36	.05628

A deviation similar to the one noted by Willard and Young is to be found in Expts. 5–7. A constant reading was attained much more slowly in Expts. 5–7 and the break at the end-point, which amounted to 180–200 mv. in Expts. 3–4, was about 140 mv. in Expt. 5 and 80–100 mv. in Expts. 6–7. Expt. 5 was run more slowly than the others. It is thus recommended that the hydrochloric acid concentration be made 4 molal when titrating arsenious acid with ceric solution using either the iodine monochloride end-point or using iodine monochloride as a catalytic agent and determining the end-point electrometrically.

Summary

Experiments have shown that by the addition of a small amount of iodine monochloride and using the iodine monochloride end-point arsenious acid can be rapidly and accurately titrated in a hydrochloric acid solution at room temperature with permanganate solutions. The effects of varying the acid from 1 to 4 molal are shown; below 2 molal the end-point is attained very slowly. The values obtained from standardizing a permanganate solution against arsenious oxide by this method are found to be in close agreement with those obtained using sodium oxalate.

It has also been shown that arsenious acid can be titrated with ceric sulfate solutions by the same method. Rapid end-points are attained if the solution is 4 molal in hydrochloric acid. Close agreement is found in standardizing a ceric solution against arsenious oxide by this method and against sodium oxalate. It has also been found that if the solution is 4 molal in hydrochloric acid, arsenious acid can be accurately titrated with ceric sulfate solutions, using iodine monochloride as a catalyst and determining the end-point electrometrically. The electrometric method is liable to error if the acid concentration is as low as 2 molal.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CESIUM BISMUTH IODIDE

BY C. C. MELOCHE AND P. V. CLARK

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In studying certain reactions of cesium it was observed that a solution of hydrogen bismuth iodide when added to one of cesium nitrate gave a bright red crystalline precipitate. On analysis it was found that this compound had the empirical formula $Cs_3Bi_2I_9$ and was, therefore, identical in composition with the compound which Wells and Foote[1] had prepared by the interaction of cesium iodide and bismuth iodide. The interesting properties of this substance and its application in the determination of cesium justify a brief description.

Reagents

Cesium Nitrate.—The method of Godeffroy[2] as modified by Wells[3] was used at first for the preparation of cesium nitrate from pollucite. Later a modification suggested by Willard and Scott was employed.

Hydrogen Bismuth Iodide Solution.—This reagent was prepared by dissolving C. P. bismuth hydroxide, bismuth basic carbonate or bismuth oxyiodide in an excess of specially purified hydriodic acid and diluting. The solution was preserved in an atmosphere of hydrogen or carbon dioxide.

Preparation and Analysis.—A dilute aqueous solution of the cesium nitrate was treated dropwise in the cold with a slight excess of the hydrogen bismuth iodide solution. When the reaction was found to be complete, the precipitate was washed by decantation with 0.1 N hydriodic acid, transferred to a Büchner funnel, washed further with 0.1 *N* hydriodic acid, then with alcohol and finally dried at 110°.

The red compound was analyzed as follows. Five-tenths to one-gram samples were dissolved in 1:5 nitric acid and the solution boiled to remove free iodine. After cooling and diluting, the bismuth was separated as bismuth sulfide, the sulfide decomposed by hot 1:4 nitric acid and the resulting solution of bismuth nitrate used for the determination of bismuth by the phosphate method as modified by Schoeller and Waterhouse.[4]

The filtrate from the bismuth sulfide was evaporated with aqua regia to remove any ammonium salts and the cesium finally converted to cesium sulfate by evaporation with sulfuric acid, treatment with ammonium carbonate and gentle ignition.

The iodine was determined volumetrically on separate samples: 0.5 to 0.6 g. was suspended in hydrochloric acid (3:2), a little chloroform

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[1] Wells and Foote, Am. J. *Sci.*, [4] 3, 461 (1897).

[2] Godeffroy, ***Ber.***, 7, 375 (1874).

[3] Wells, ***Am. Chem. J.***, 26, 266 (1901).

[4] Schoeller and Waterhouse, Analyst, 45, 436 (1920).

added and the iodine titrated with 0.025 M potassium iodate solution in carbon dioxide atmosphere as recommended by Andrew.[5]

The averages of closely agreeing analyses were as follows: 20.66% Cs, 21.28% Bi and 58.15% I. The values calculated for $Cs_3Bi_2I_9$ were 20.34% Cs, 21.34% Bi and 58.32% I.

Properties.—On examination under the microscope the crystals are transparent and appear to be hexagonal. Gradual hydrolysis occurs when the compound is suspended in water at room temperature, and in boiling water the insoluble copper colored bismuth oxyiodide, together with the soluble cesium iodide and hydriodic acid, is rapidly formed. Hydriodic acid in concentrations as low as 0.05 N will prevent hydrolysis at 25°. The red compound dissolves to some extent in dilute hydrochloric acid and is completely decomposed by boiling 1:5 nitric acid with evolution of iodine. Strong nitric acid converts some of the iodide to iodate and causes the precipitation of white finely divided bismuth iodate.

The approximate solubility in different solvents was determined by sealing the solvent with excess of the red compound in a 200-ml. glass tube otherwise filled with carbon dioxide. After agitation for at least forty-eight hours in a thermostatic tank kept at 25 ± 0.01°, the remaining cesium bismuth iodide was allowed to settle, the glass tube opened and 10-ml. portions of the clear supernatant liquid were removed for the colorimetric determination of bismuth by the bismuth iodide method. The free iodine which was almost invariably present in the solvent at the end of the solubility determination was determined by means of 0.01 *N* thiosulfate. The results obtained are recorded in Table I.

TABLE I

APPROXIMATE SOLUBILITIES OF CESIUM BISMUTH IODIDE

Solvent at 25°	Free iodine, g. per 100 ml.		$Cs_3Bi_2I_9$ diss., g. per 100 ml.		Cs equivalent g. per 100 ml.	
0.1096 N hydriodic acid	<0.00066	**0.0000**	0.170	**0.166**	**0.035**	**0.034**
0.0472 N hydriodic acid	.0000	**< .00066**	.094	.082	.019	.017
Absolute alcohol	.006	.010	.00078	.00073	.00016	.00015

It will be observed that the solubility of $Cs_3Bi_2I_9$ increases with increase in concentration of hydriodic acid. The solubility in absolute ethyl alcohol corresponds to less than 0.2 mg. of cesium per 100 ml. The solubility in mixtures of absolute ethyl alcohol and absolute n-butyl alcohol is also very low.

The effect of drying and igniting cesium bismuth iodide at various temperatures was studied in some detail on account of the application of this data in analytical work. As a rule 0.5 to 1.0-g. samples of cesium bismuth iodide were transferred to porcelain boats and placed in a pyrex glass tube enclosed by a constant temperature electric oven. A slow

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[5] Andrew, THIS JOURNAL, **25**, 756 (1903).

current of air dried by means of concentrated sulfuric acid was passed through the glass tube. At the higher temperatures a porcelain tube heated by helically wound resistance wire was employed. The temperature was controlled by a rheostat and measured by means of a platinum iridium thermocouple. The losses at various temperatures are shown in Table II.

TABLE II

LOSS IN WEIGHT OF CESIUM BISMUTH IODIDE ON HEATING IN DRY AIR

$Cs_3Bi_2I_9$ g.	Temp.. °C.	Time, hours	Loss in weight, g.	Rate of loss in weight, % per hour
0.8343	210	13.5 additional	0.00035 additional	0.003
0.8343	250	3.0 additional	0.0009 additional	0.036
1.3289	300	12.0 total	0.0625 additional	0.392
0.8237	400	19.0 additional	0.2767 total	1.768
1.5578	750	49.0 additional	1.1590 total	...

The sensible constancy in weight at 210 and at 220° after the initial loss of hygroscopic moisture, as well as the slow losses at 230° and above, are shown in Table III.

TABLE III

THE STABILITY OF CESIUM BISMUTH IODIDE AT 210°

Weight of $Cs_3Bi_2I_9$ after drying at 110°: (I) 0.8343, (11) 1.3496.

Temp., °C.	Time, hours	Loss in weight, g.		Loss in weight, % per hour	
		(I)	(II)	(I)	(II)
210	3.0 i	0.00075	0.0010	0.030	0.025
210	3.0 a	.00010	,0002	.004	.005
210	3.0 a	.00005	00015	.002	.004
210	7.5 a	.0002	,00025	.003	,0025
220	3.0 a	.0000	.0000	.000	.000
230	3.0 a	.0004	0002	.016	.005
240	3.0 a	.0010	.0002	.040	.005
250	3.0 a	.0009	.0013	.036	.032

i = initial heating. a = additional.

When cesium bismuth iodide was heated in dry air as above described, the color changed to a dark red or very dark brown when the temperature was 110 to 210°, but the original bright red color was restored on cooling. At temperatures above 230° loss of iodine occurred and a permanent change in color eventually took place. At first an orange-colored material was produced. After heating for sixty-two hours at 300° the residue was lemon-yellow. After heating for twenty to thirty hours at 400° a white or yellowish-white material remained. Several specimens of this white material were prepared, the percentage loss in weight observed and the iodine content determined volumetrically. The averages of closely agreeing results were as follows: loss in weight of the red precipitate, 33.65%; iodine in residue, 22.41%, referred to the red precipitate;

iodine replaced by oxygen, 35.91% of the red precipitate; iodine replaced calculated from loss in weight, 35.91% of the red precipitate; atoms of iodine replaced, 5.54. The white substance, though not of definite composition, was obviously formed by the replacement of nearly six of the nine original atoms of iodine by an equivalent of oxygen. The composition, therefore, tends toward the limit expressed by the formula $Bi_2O_3\cdot 3CsI$, but neither the pure white color nor the sensible constancy in weight is a reliable indication that this limit has been reached.

The use of cesium bismuth iodide in the quantitative determination of cesium is being investigated.

The authors wish to express their appreciation of the interest which Professor H. H. Willard has taken in the progress of this work.

Summary

1. A new method for the preparation of cesium bismuth iodide has been described and the properties of cesium bismuth iodide, which have significance in analysis, have been studied.

2. The very low solubility in ethyl alcohol, the constancy in weight at 210°, and the quantitative reaction with standard potassium iodate have been noted.

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

STUDIES ON THE THERMOCHEMISTRY OF THE COMPOUNDS OCCURRING IN THE SYSTEM $CaO-Al_2O_3-SiO_2$. III. THE HEAT OF HYDRATION OF CALCIUM OXIDE[1]

BY T. THORVALDSON, WELDON G. BROWN AND C. R. PEAKER

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Introduction

Several values for the heat of hydration of calcium oxide are to be found in the literature. Thomsen[2] obtained the value 15,540 calories per mole at 20° from data on the heat of solution of calcium oxide and calcium hydroxide in $HCl\cdot 300H_2O$. Berthelot[3] determined the heat of solution of calcium oxide in hydrochloric acid (one-sixth molal) at 16°, the heat of solution of calcium hydroxide in water and the heat of neutralization of a solution of calcium hydroxide by 0.5 M hydrochloric acid. From these results he calculated the heat of hydration of calcium oxide, obtaining the

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[1] The authors wish to acknowledge generous financial assistance from the National Research Council of Canada.

[2] Thomsen, "Thermochemische Untersuchungen," Vol. 3, 1883, p. 248.

[3] Berthelot, Ann. *chim. phys.*, [5] 4, 531 (1875).

value 15,100 calories per mole. Kohlschiitter and Feitknecht[4] obtained the value 15,300 calories per mole at 20° by measuring directly the heat of hydration of calcium oxide in boiled water using a Dewar flask as a calorimeter. Roth and Chall,[5] using a calorimeter with a reaction vessel of porcelain designed for work at higher temperatures, obtained 15,440 calories per mole at 50° from determinations of the heats of solution of calcium oxide and calcium hydroxide in $HCl \cdot 24.65H_2O$ at this temperature, Calculating the temperature coefficient of the reaction from the difference in the heat capacities of the factors and products (7.65 calories per mole per degree between 20 and 50") and applying this correction, one obtains 15,210 calories per mole at 20°. These authors also quote a determination by Dragert which gave the value 15,175 calories per mole at 15°.

The value obtained by the direct hydration of calcium oxide in water is probably affected slightly by the heat of solution of calcium hydroxide in the water. It should further be noted that values for the heat of hydration obtained by the direct and the indirect methods are not directly comparable. The result obtained by the former method may be considered to include the heat of wetting of the resulting calcium hydroxide in lime water. When the latter method is used, the heat of solution of the calcium hydroxide, which includes the total surface energy of the material, is subtracted from the heat of solution of calcium oxide. One would, therefore, expect the value obtained by the indirect method to be lower than the value obtained by the direct method, the difference being equal to the heat of wetting of the calcium hydroxide. Variations in the heat of wetting[6] of different samples of calcium hydroxide indicate that the value for the surface energy may vary considerably according to the method of preparation. The effect of such factors as these has not been considered in previous determinations of the heat of hydration of calcium oxide.

The surface energy of the calcium oxide appears in the value for the heat of hydration determined by either method. It is possible that this may also vary, although the constancy of the heat of solution of calcium oxide prepared from calcite by ignition at different temperatures[7] and the close agreement between the values for the heat of solution of calcium oxide prepared from calcium oxalate, calcite and aragonite[7] indicates fair constancy for calcium oxide prepared by the methods in common use.

Apparatus **and** Experimental Procedure.—The calorimeter, which was of the Richards adiabatic type with a slight modification, the Beckmann thermometers, the method of introducing the sample into the calorimeter and the limits of adiabatic control have been described in the first and

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[4] Kohlschiitter and Feitknecht, *Helv. Chim. Acta*, 6, 359 (1923).

[5] Roth and Chall, *Z. Elektrochem.*, 34, 185 (1928).

[6] Thorvaldson and Brown, THIS JOURNAL, 52, 80 (1930).

[7] Thorvaldson, Brown and Peaker, *ibid.*, 51,2678 (1929).

second papers of this series.[6,7] A copper calorimeter vessel lined with gold was used for these determinations, the hydrating liquid being saturated lime water in order to avoid the thermal effect due to solution of lime.

Specific Heats.—The values used in calculating the heat capacity of the calorimeter system were: copper,[8] 0.092; gold,[8] 0.031; gold alloy (80% Au, 20% Cu),[8] 0.044; CaO,[8] 0.19. All weights were corrected to vacuum.

The specific heat of saturated lime water over the temperature interval 18–20' was determined by the method of Richards and Rowe? Four determinations gave the values 0.9980, 0.9971, 0.9979 and 0.9987, or a mean of 0.9979. The value 0.998 was used in the calculations.

Purification of Materials

Saturated Lime Water.—Excess of pure calcium oxide was shaken with freshly redistilled carbon dioxide-free water. The saturated solution was allowed to stand in contact with excess of calcium hydroxide and was protected from contamination with carbon dioxide.

Calcium Oxide.—The procedure used for the preparation of pure calcium oxide and the precautions taken to assure purity of reagents were described in the first paper of this series.'

Samples A and B.—Commercial "precipitated" calcium carbonate was dissolved in freshly redistilled nitric acid. The neutral solution was treated with excess of bromine and milk of lime, boiled, filtered and the calcium nitrate recrystallized four times. Sample A was prepared by precipitating the calcium as oxalate from a dilute solution of the nitrate with recrystallized ammonium oxalate. Sample B was prepared by a double precipitation as calcium carbonate (calcite) with redistilled ammonium carbonate.

Sample C.—This was prepared from a very pure sample of recrystallized calcium chloride by precipitation as calcium carbonate (calcite) from a 1% solution of the chloride with freshly redistilled ammonium carbonate.

Sample D.—Calcium nitrate was recrystallized eight times and the calcium then precipitated as calcium carbonate (calcite).

Calcium oxide was prepared from these samples as required by ignition to constant weight in platinum in a muffle furnace.

Determination of the Heat of Hydration of CaO.—Of some twenty samples of pure calcium oxide prepared, only five were found to hydrate completely in the calorimeter within one hour. Samples prepared from minutely crystalline calcium carbonate (calcite) or from samples containing an appreciable amount of the spherulitic form, had a tendency to cake slightly on ignition and were found to hydrate more slowly than samples prepared from more coarsely crystalline calcite which generally did not cake. In the case of the more coarsely crystalline materials, the rate of hydration could in some cases be increased by grinding the sample before ignition, but prolonged grinding resulted in caking on ignition and consequently in a slower rate of hydration.

[8] "International Critical Tables," 1929, Vol. V, pp. 88, 91, 92, 120.

[9] Richards and Rowe, *Proc. Am. Acad.*, 49, 191 (1913).

TABLE I

DIRECT DETERMINATION OF THE HEAT OF HYDRATION OF CALCIUM OXIDE

"Water equivalent" of apparatus	18.47 cal./deg.
500.3 g. saturated lime water	499.3 cal./deg.
Total heat capacity—Expts. 1–8	517.8 cal./deg.
Total heat capacity—Expts. 9–11	517.2[a] cal./deg.

Expt.	Sample of CaO	CaO, g.	Final temp., °C.	Time, min.	Temp. rise,[b] °C.	Heat of hydration. 20° cal. per g. of CaO
1	A	3.9829	19.98	20	2.127	276.5
2	A	3.9372	20.27	16	2.100	276.2
3	B	3.8993	20.24	40	2.085	276.9
4	B	3.9853	20.24	36	2.133	277.1
3	C	3.8798	19.81	42	2.066	275.7
6	C	3.7524	19.93	48	1.999	275.9
7	C	3.6393	20.08	32	1.938	275.7
8	C	3.7004	19.95	14	1.973	276.0
9	D	3.7517	20.03	16	2.007	276.7
10	D	3.7982	20.07	14	2.046	278.6
11	D	3.6391	20.10	16	1.416	277.5
Average			20.06"			276.6
Corrected for evaporation						276.8

[a] In Expts. 9, 10 and 11 a different Beckmann thermometer with a 0.6 cal./deg. lower water equivalent was used. [b] These values are corrected for (1) stirring, (2) stem exposed, (3) setting of thermometer and (4) variation in temperature of CaO from 20° at time of introduction into the calorimeter.

As the solubility of calcium hydroxide decreases with rising temperature, one might expect this substance to separate out with absorption of heat during the determination of the heat of hydration. It was, however, found that some calcium oxide dissolves, producing a supersaturated solution. This is in agreement with the observation of Miller and Witt,[10] who found that when calcium oxide is shaken with water in excess of the amount required to form the hydroxide, a supersaturated solution results, the maximum concentration being reached in about four hours, after which it diminishes very gradually, a saturated solution not being obtained until after shaking for more than twenty-four hours.

The amount of supersaturation varied with different samples of calcium oxide. With a sample which hydrated slowly, the supersaturation one-half hour after the introduction of the sample of CaO was found by titration to be 3%, while with three samples which hydrated quickly (in about ten minutes) it was found to be 10.6, 11.0 and 11.7%, respectively. Determination of the supersaturation by the conductivity method gave a somewhat lower value. Both this and the marked tendency of the particles of lime to pass through the filter paper suggests that a part of the supersaturation as determined by titration may have been due to colloid

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[10] Miller and Witt, *J. Phys. Chem.*, 33, 285 (1929).

particles of calcium hydroxide. From the average value of the determinations of supersaturation made, it appears that a correction of 0.5 cal. per gram of CaO should be applied to the value in Table I as a correction for heat of solution.

Applying this correction, the value for the isothermal heat of hydration of calcium oxide at 20° becomes 276.3 $\text{cal.}_{20°}$ per gram or 15.49 kg. $\text{cal.}_{20°}$ (64.76 kj.) per mole.

Calculation of the Heat of Hydration of CaO from the Heats of Solution of CaO and $Ca(OH)_2$ in $HCl{\cdot}200H_2O$.—The heat of solution of calcium oxide in $HCl{\cdot}200H_2O$ at 20° was found to be 829.2 $\text{cal.}_{20°}$ per gram,[7] and the corresponding value for calcium hydroxide, less the heat of wetting of the hydroxide in saturated lime water, was found to be 550.3 $\text{cal.}_{20°}$ per gram of CaO.[6] Subtracting the second value from the first gives the figure 278.9 $\text{cal.}_{20°}$ per gram for the heat of hydration of calcium oxide at 20°. This figure is 2.6 cal. per gram in excess of the value obtained above by direct hydration of CaO in saturated lime water.

In searching for the cause of this discrepancy one observes that the ratio of calcium oxide to hydrochloric acid used in the determinations of the heat of solution of calcium hydroxide was lower than that used in the determination of the heat of solution of calcium oxide. Determinations were, therefore, made of the heat effect produced on mixing $HCl{\cdot}200H_2O$ with the final solution obtained in determining the heat of solution of calcium oxide in $HCl{\cdot}200H_2O$.[7] No heat effect was observed, so that no error had been introduced from this source.

Microscopic examination of the calcium oxide and calcium hydroxide suggested a possible explanation of the discrepancy. It was found that the particles of calcium oxide retained the shape and the size of the original calcite crystals from which they were made. During hydration and for some time after the temperature of the calorimeter reached apparent constancy, physical changes occurred, the rate of these changes varying with different samples of calcium oxide. In the case of samples hydrating rapidly, the particles broke up into very small fragments during the hydration; in other cases this process was very slow, gradual accumulation of minute globules in the liquid and on the surface of the large particles being observed. M. v. Glasenapp[11] describes the production of colloidal hydrated lime by exposing a material containing free CaO to water. The "droplets" shown in the photographs published by v. Glasenapp, some free in the liquid and others attached to the larger aggregates, appear to be similar to the small rounded particles described above.

It is possible that during the first step of the hydration of calcium oxide in lime water, colloidal calcium hydroxide is formed and the calorimetric measurements give the heat effect for this reaction. The very slow changes

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[11] M. v. Glasenapp, *Kolloid-Z.*, 31, 195 (1922).

in the physical condition of the particles which continue for a long time may be accompanied by the evolution of appreciable quantities of heat, thus explaining the low value obtained in measuring directly the heat of hydration.

Summary and Conclusions

1. The value 276.3 cal.$_{20°}$ per gram or 15.49 kg. cal.$_{20°}$ (64.76 kj.) per mole was obtained for the heat of hydration of CaO in saturated lime water at 20°.

2. This value is 2.6 cal. per gram lower than the value (278.9 cal.$_{20°}$ per gram, 15.64 kg. cal.$_{20°}$ per mole) obtained by calculation from the heats of solution of calcium oxide and calcium hydroxide in $HCl{\cdot}200H_2O$.

3. Microscopic examination indicated that physical changes in the hydrated material continue for a long time after the temperature of the calorimeter comes to apparent constancy. It is suggested that changes in the energy of surface and of crystal lattice may be responsible for the discrepancy between the observed and calculated results for the heat of hydration of calcium oxide.

SASKATOON, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

IONIC RATIOS IN THE WATERS OF THE NORTH PACIFIC OCEAN[1]

BY THOMAS G. THOMPSON AND CALVERT C. WRIGHT

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During the past sixty years a number of papers[2] have appeared giving the analyses of sea water from various regions of the world. From some of these data the ratios of the various ions occurring in the waters of the several oceans may be calculated. Such ratios give valuable information as to the constancy of composition of sea water; and, once established and referred to the chlorinity[3] as unity, may be used to calculate the con-

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[1] Paper read before the Pacific Intersectional meeting of the American Chemical Society held at Berkeley, California, June 21, 1929.

[2] (a) Thorpe and Morton, *Ann.*, 158, 122 (1871); (b) Dittmar, "Reports of H. M. S. "Challenger," *Phys. and Chem.*, 1884, Vol. 1; (c) Schmidt, *Bull. Acad. St. Petersburg*, 24, 231 (1878); (d) Schmelck, "Den Norske Nordhavs-Exped.," Part 9, 1882, p. 1; (e) Forsberg, "Vega Exped. Rept.," 1883, Vol. 2, p. 376; (f) Kolotoff, *J. Russ. Phys.-Chem. Soc.*, **24**, 82 (1893); (g) Makin, *Chem. News*, 77,155 (1898); (h) Natterer, *Monatsh.*, 13, 873 (1892); 14, 624 (1893); 15, 530 (1894); 16, 405 (1895); 20, 1 (1899); 21, 1037 (1900); (i) Schloesing, *Compt. rend.*, 142,320 (1906); (j) Coppock, *Chem. News*, 96, 212 (1907); (k) Wheeler, THIS JOURNAL, 32,646 (1910); (l) Bertrand, *Compt. rend.*, 174, 1251 (1922).

[3] The chlorinity of sea water is defined as the number of grams of chloride ions contained in a kilogram of water, assuming that the small amounts of bromide ions and traces of iodide ions have been converted to chlorides.

centrations of the several ions when only the chlorinity of the water is known. The constancy of the sulfate chlorinity ratio was recently demonstrated for the waters of the North and Northeast Pacific.[4]

In the present investigation special attention has been given to the calcium and magnesium ions in the waters of this same region. A critical examination was first made of the different methods used in the determination of calcium and magnesium ions in sea water and the most accurate methods accordingly adopted.

After a study of the literature, particularly the conclusions of Giral,[5] and considerable laboratory experience, the authors became convinced that many of the discrepancies in the calcium–magnesium ratios calculated from the data of other investigators were due to faulty methods of analysis, or to the tendency of investigators to report results to a degree of accuracy not warranted by evident experimental errors.

Methods of Analysis

To ascertain the most accurate method for the determination of calcium and magnesium in sea water, standard solutions of pure magnesium sulfate and calcium chloride were prepared. These solutions were used in the preparation of a synthetic sea water, in which only carefully purified and analyzed chemicals entered. This water had the following composition

Mg^{++}	$1.1506\,^0/_{00}$	Na^{+}	$13.0\,^0/_{00}$
Ca^{++}	$0.3750\,^0/_{00}$	Cl^{-}	$17.0\,^0/_{00}$
K^{+}	$0.37\,^0/_{00}$	$SO_4^{=}$	$4.6\,^0/_{00}$

Throughout all of the analytical work the following precautions were taken: (a) every reagent was tested for its purity; (b) ignitions were all made in platinum crucibles; (c) constant weight was considered to have been obtained only when three weighings checked to within 0.1 milligram; (d) all weighings were made at constant temperature.

Determination of Calcium.—In previous determinations of calcium in sea water, the oxalate method with ignition of the precipitate to the oxide has been exclusively used. The chief variation in the method has been the number of precipitations of the calcium oxalate. In a few instances only one precipitation was used but in the majority of cases three or the equivalent were considered necessary. Thus Dittmar used a single precipitation for individual samples, but combined the ignited calcium oxide precipitates, analyzed them by double precipitation and corrected the original results. Natterer used a double precipitation but boiled the second precipitate with dilute ammonium oxalate solution.

The data presented in Table I demonstrate that at least three precipitations of the calcium oxalate are necessary.

[4] **Thompson, Lang and Anderson,** *Publ. Puget Sound Biol. Sta*, **5, 277–292 (1927).**

[5] **Giral,** *Mem. Inst. Español de Ocean*, 2, 199 (1924).

TABLE I

DATA ON THE PRECIPITATION OF CALCIUM OXALATE

		Grams of Ca per kilo of synthetic sea water				
		a	b	c	Mean	Variation
Calcium present		0.3750	0.3750	0.3750	0.3750	
Calcium found	Two pptns.	.3809	.3800	.3817	.3809	+0.0059
	Three pptns.	.3752	.3760	.3749	.3755	+ .0005

Titration of the calcium oxalate with potassium permanganate yielded varying results as shown by Hahn and Weiler[6] and accordingly was not considered. The determinations of calcium in samples of filtered sea water were carried out in much the same manner as that described by Fales.[7] Two hundred and fifty grams of the sea water was used, three precipitations of the calcium oxalate were made and the latter was finally ignited at a high temperature in an electric muffle to constant weight.

Determination of Magnesium.—The hydroxyquinoline method of Berg[8] and its modification for sea water by Matthews and Ellis[9] were studied. It was found that this procedure was far less accurate than Epperson's[10] modification of the magnesium ammonium phosphate method.

Previous workers in determining magnesium in sea water by the phosphate method considered two and in some cases one precipitation sufficient. The data of Epperson and the results reported in Table II show the fallacy of this assumption. Due to the peculiar composition of sea water, three precipitations of the magnesium ammonium phosphate are essential.

TABLE II

COMPARISON OF DIFFERENT METHODS AND MODIFICATIONS FOR THE DETERMINATION OF MAGNESIUM

	Grams of Mg per kilo of synthetic sea water				
	a	b	c	Mean	Variation
Magnesium present	1.1506	1.1506	1.1506	1.1506	
Determined by Epperson's Method					
Two precipitations	1.162	1.149	1.157	1.156	+0.005
Three precipitations	1.149	1.152	1.152	1.151	.000
Determined by Berg's Method					
Two precipitations and drying 4 hrs. at 100°	1.206	1.250	1.170	1.211	+ .060
Matthews and Ellis' Modification					
Drying 2 hrs. at 100°	1.191	1.174	1.198	1.188	+ .037
Drying 6 days at 100°	1.169	1.155	1.181	1.168	+ .017

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[6] Hahn and Weiler, *J. prakt. Chem.*, **70**, 1 (1927).

[7] Fales, "Inorganic Quantitative Analysis," The Century Co., New York, 1925, p. 198.

[8] Berg, *Z. anal. Chem.*, **71**, 23 (1927).

[9] Matthews and Ellis, *J. du Conseil*, 3, 191 (1928).

[10] Epperson, THIS JOURNAL, 50, 321 (1928).

This conclusion is partially corroborated by Bertrand,[11] who obtained high results on a synthetic sea water using only two precipitations.

The assertion made by several investigators[9,12] that a large error due to the solubility of the magnesium ammonium phosphate may enter into the determination seems to be unfounded, especially for Epperson's modification. The data given below were obtained from nine analyses of a solution of pure magnesium chloride containing 0.0919 grams of magnesium per kilo.

	a	b	c
1 Precipitation	0.0919	0.0919	0.0918
2 Precipitations	.0918	.0918	.0921
3 Precipitations	.0920	.0920	.0918

These data show that no error of solubility is introduced.

In determining the magnesium in sea water aliquot parts by weight of the filtrate from the calcium determination were taken and Epperson's procedure was followed, using three precipitations.

Source of Samples of Waters Studied

Puget Sound Biological Station, Friday Harbor, Washington.—The Puget Sound Biological station is situated in the San Juan Archipelago about 80 miles north of Seattle. From September, 1926, to September, 1928, samples of water were collected weekly at the surface and at a depth of 12.5 meters. Composite samples of about 2.5 liters, for each month, were made from the weekly samples, and used in the present investigation.

East Sound, San Juan Archipelago, Washington.—East Sound is an estuary about 10 miles in length, and its waters are characterized by an exceedingly rich diatom growth. Gran and Thompson[13] found as many as 1400 cells per milliliter of water. During the period of rich growth, 25 samples were collected from various parts of the sound and from these a composite sample was prepared.

Nanaimo Bay, British Columbia.—A 4-liter sample was collected through the courtesy of Professor Hutchinson of the University of British Columbia. The waters of the bay had a chlorinity much less than those of any region studied, resulting from the dilution of the waters of the Gulf of Georgia by the Fraser River.

Gulf of Alaska.—In 1928 a composite sample was made from 120 samples collected by the International Fisheries Commission at ten-mile intervals out from Ocean Cape, Cape Cleare and Cape Chiniak, Alaska, at depths varying between the surface and 1000 meters.

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[11] Bertrand, *Compt. rend.*, 174, 1251 (1922).

[12] Schmelck, "Den Norske Nordhavs-Exped.," Part 9, 1882, p. 1; Seidell, "Solubility of Inorganic Substances," 2d ed., D. Van Nostrand Company, New York., 1919,

[13] Gran and Thompson, "Publ. Puget Sound Biol. Sta.," in press.

In 1929 three samples were collected for the authors in the Gulf of Alaska. No. 16 was taken at the surface, 14 miles from the coast, No. 370 was obtained at a depth of 1200 meters about 250 miles from shore, while No. 406 was taken at a depth of 375 meters, 45 miles south of Kodiak Island.

All of the samples described above were analyzed carefully for calcium and magnesium ions, and for chlorinity. The latter was determined by the method previously described by one of us.[14] The results obtained, together with the ratios calculated therefrom, are given in Table III.

TABLE 111

ANALYSES AND IONIC RATIOS OF THE WATERS OF THE NORTH AND NORTHEAST PACIFIC OCEAN

Samples		Chlorinity,	Mg,	Ca,	Ratios		
Source	Description	grams/kilo	grams, per kilo	grams, per kilo	Mg/Cl	Ca/Cl	Ca/Mg
Friday Harbor	Sept. '26	16 95	1.134	0.3640	0.06690	0.02144	0.3211
Friday Harbor	Oct. '26	17 18	1.147	.3681	.06676	.02143	.3209
Friday Harbor	Nov. '26	16 98	1.136	.3646	.06690	.02147	.3210
Friday Harbor	Dec. '26	17 02	1.140	.3673	.06698	.02158	.3222
Friday Harbor	Jan. '27	16 81	1.125	.3614	.06692	.02150	.3212
Friday Harbor	Feb. '27	16 83	1.125	.3608	.06687	.02144	.3206
Friday Harbor	Mar. '27	16 78	1.124	.3598	.06698	.02144	.3201
Friday Harbor	Apr. '27	16 96	1.134	.3640	.06686	.02146	.3216
Friday Harbor	May '27	17 11	1.141	.3676	.06669	.02148	.3222
Friday Harbor	June '27	16 98	1.139	.3655	.06708	.02153	.3209
Friday Harbor	July '27	16 54	1.107	.3562	.06696	.02154	.3216
Friday Harbor	Aug. '27	16 29	1.093	.3503	.06710	.02150	.3205
Friday Harbor	Sept. '27	No sample	...	...	....	....	...
Friday Harbor	Oct. '27	16 90	1.133	.3626	.06704	.02146	.3201
Friday Harbor	Nov. '27	16 81	1.128	.3612	.06710	.02149	.3202
Friday Harbor	Dec. '27	16 37	1.097	.3502	.06701	.02139	.3192
Friday Harbor	Jan. '28	16 38	1 097	.3508	.06700	.02142	.3196
Friday Harbor	Feb. '28	16 58	1.108	.3568	.06686	.02152	.3219
Friday Harbor	Mar. '28	16 85	1.127	.3627	.06691	.02153	.3217
Friday Harbor	Apr. '28	16 86	1.132	.3633	.06711	.02155	.3209
Friday Harbor	May '28	16 65	1.115	.3589	.06697	.02156	.3219
Friday Harbor	June '28	16 25	1.085	.3504	.06675	.02156	.3229
Friday Harbor	July '28	16 38	1.097	.3528	.06697	.02154	.3216
Friday Harbor	Aug. '28	16 90	1.130	.3618	.06686	.02141	.3202
East Sound	Comp. '28	16 44	1.101	.3549	.06700	.02159	.3220
Nanaimo Bay, B. C.	Comp. '29	14 21	0.9521	.3070	.06700	.02160	.3224
Gulf of Alaska	Comp. '28	18 12	1.214	.3883	.06700	.02143	.3199
Gulf of Alaska	No. 16 '29	17 83	1.191	.3834	.06680	.02150	.3219
Gulf of Alaska	No. 370 '29	19 09	1.280	.4121	.06705	.02159	.3220
Gulf of Alaska	No. 406 '29	18 79	1.257	.4054	.06690	.02158	.3225
			Average		.06694	.02150	.3212
			Maximum		.06711	.02160	.3229
			Minimum		.06669	.02139	.3192
			Difference		.00042	.00021	.0037

Discussion

The authors claim a maximum experimental error less than 0.0015 g. of magnesium, 0.0006 g. of calcium and 0.015 g. chlorinity per kilo of water. Based on these limits, the variations in the ratios resulting from experi-

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[14] Thompson, THIS JOURNAL, **50, 681 (1928).**

mental error were calculated to be 0.00011 for Ca/Cl, 0.00020 for Mg/Cl and 0.0016 for Ca/Mg. Of the 30 samples studied, only 2 showed values outside these limits of error. The errors in the method used by Matthews and Ellis, as shown by their results, are far greater than any variations in the composition of the sea waters examined by the authors. Thus, assuming Mg/Cl as 0.06692 and a chlorinity of $17.00^0/_{00}$, the experimental error of their method would give a variation from 0.0661 to 0.0677, or a maximum difference of 0.0016.

From the data of Johnston[15] the ionic ratios for the fresh water of the Fraser River were calculated to be 0.484 Mg/Cl, 2.719 Ca/Cl and 5.618 Ca/Mg, which is an interesting contrast for those obtained on sea water. Using Johnston's data and assuming a sea water with a chlorinity of $17.00^0/_{00}$ the effect of dilution by the Fraser River would produce the following very slight changes in the ionic ratios.

	Ca/Cl	Mg/Cl	Ca/Mg
Sea water, $17.00^0/_{00}$ Cl	0.02150	0.06692	0.3211
Sea water diluted by Fraser River to $14.00^0/_{00}$ Cl	.02165	.06694	.3234

TABLE IV

IONIC RATIOS OF OTHER INVESTIGATIONS

Worker	Source	Date	Number of samples	Ca/Mg = K	Ca/Cl = K	Mg/Cl = K
Thorpe	Irish Sea	1871	1	0.3351	0.02183	0.06528
Schmidt[a]	White Sea	1878	3	.3185	.02189	.06873
Schmidt"	Arctic Ocean	1878	2	.3103	,02095	.06753
Schmidt[a]	Straits of Malacca	1878	1	.2915	.02143	.07259
Schmidt[a]	China Sea	1878	1	.3132	.02145	.06758
Schmidt[a]	Indian Ocean	1878	2	.3120	.02091	,06685
Schmelck"	North Atlantic	1882	51	.3151	.02182	.06926
Forsberg	Siberian Ocean	1883	4	.3089	.02128	.06889
Dittmar[a]	All oceans	1884	77	.3171	.02162	.06815
Natterer[a]	Mediterranean Sea	1892	42	,3183	,02162	.06971
Natterer[a]	Sea of Marmora	1895	44	....	,02197	.....
Natterer[a]	Red Sea	1896	15	.3167	.....	.....
Kolotoff	Black Sea	1896	4	,3348	.02177	.06512
Schloesing	Mediterranean Sea	1906	1 .	,3370	,02228	.06612
Schloesing	Mediterranean Sea	1906	1	.3462	.02266	.06546
Schloesing	Atlantic Ocean	1906	1	.3441	.02303	,06693
Steiger	Gulf of Mexico	1910	1	.3348	,02205	.06490
Wheeler	West Atlantic	1910	5	.3297	.02208	.06697
Bertrand	Atlantic Ocean	1922	1	.3319	.02092	.06302
Bertrand	Mediterranean Sea	1922	1	.3299	.02133	.06465
	Mean average			.3243	.02177	.06713
	Weighted average		258	.3178	.02172	.06859
	Thompson and Wright			.3212	.02150	.06694

[a] Corrected for gravimetric factors used due to change in atomic weight.

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[15] Johnston, "Canada Dept. of Mines, Geol. Sur., Memoir, 125," No. 107, p. 25 (1921).

In Table IV are shown the results obtained for the ionic ratios calculated from the data of other investigators. A comparison of either of the ratios involving magnesium is hardly justifiable, since the methods of analysis are open to criticism in the light of Epperson's work. For the Ca/Cl, however, several workers, with samples from widely scattered sources, obtained values agreeing with those found by the authors.

Conclusions

1. A study of the methods of analysis for calcium and magnesium in sea water has been made. The gravimetric calcium oxalate method and Epperson's modification of the magnesium ammonium phosphate method are the most accurate. Because of the large quantities of interfering ions, three precipitations are necessary for both the calcium and magnesium determinations.
2. The constancy of composition of the waters of the North and Northeast Pacific with reference to the calcium and magnesium ions and the chlorinity has been demonstrated.
3. The ratio for calcium chlorinity is 0.02150, for magnesium chlorinity 0.06694 and for calcium–magnesium 0.3212. The amounts of calcium and magnesium per kilo of sea water may be very closely estimated by multiplying the chlorinity by these factors.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

THE DISSOCIATION CONSTANT OF WATER FROM AN EQUILIBRIUM INVOLVING MERCURIC OXIDE AND MERCUROUS BROMIDE[1]

BY ROY F. NEWTON AND M. G. BOLINGER

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Introduction

The dissociation constant of water has usually been determined by one of three methods: by measurement of the conductivity of water, by determining the hydrolysis of salt solutions, or by finding the e.m.f. of cells. Possibly the best determination by conductivity measurements is that of Kohlrausch and Heydweiller[2] on the conductivity of water. It is rather difficult to estimate the magnitude of the uncertainty of their result, but their method of extrapolation from their best water to the conductivity of pure water would seem to introduce an uncertainty of 5% or more in

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[1] From a thesis submitted by M. G. Bolinger to the Graduate School of Purdue University in partial fulfilment of the requirements for the Degree of Master of Science.

[2] Kohlrausch and Heydweiller, Z. *physik. Chem.*, 14, 330 (1894); *Ann. Physik,* [4] **28,** 503 (1909).

the dissociation constant. Lewis and Randall[3] by calculation from the e.m.fs. of cells, obtain a vaiue differing by about 3% from that of Kohlrausch and Heydweiller. Lewis and Randall[3] state that the measurements by hydrolysis involve uncertainties of 10 to 20% in the assumptions alone.

The values obtained by e.m.f. measurements may be in error by 2 to 3% due to uncertainties in correction for liquid junction potentials. It would seem desirable to check the dissociation constant of water by an e.m.f. method which does not involve liquid junction potentials. A determination of the equilibrium between Hg(l), HgO(s), Br^-, Hg_2Br_2(s), and OH^- according to the reaction

$$^1/_2\, HgO(s) + {}^1/_2\, Hg(l) + {}^1/_2\, H_2O(l) + Br^- = {}^1/_2\, Hg_2Br_2(s) + OH^-$$

has been carried out in order to make possible the employment of the existing measurements of the potential of the mercury–mercuric oxide electrode[4] and of the potential of the mercury–mercurous bromide electrode[5] in the calculation of the dissociation constant of water.

Preparation of Materials

Mercury was washed in a column of nitric acid and distilled under reduced pressure in a slow current of air.

Mercurous bromide was prepared by adding potassium bromide in slight excess to a solution of mercurous nitrate which had been prepared from c. p. nitric acid and the purified mercury. The precipitate was washed three or four times by decantation, filtered and dried at 105°. The product was free from acid and soluble bromides. It was stored in dark bottles and kept away from strong light.

Mercuric oxide was prepared by heating a good c. p. product until small globules of mercury appeared. T. F. Buehrer in an unpublished investigation has shown that such mercuric oxide gives the same e.m.f. in a mercury–mercuric oxide half cell as that obtained by Ming Chow.

Potassium bromide was purified by three recrystallizations. The potassium bromide solutions were standardized by Volhard's method against silver nitrate, which had been checked against standard sodium chloride.

The sulfuric acid used for titrating the hydroxide in the equilibrium mixtures was standardized against sodium carbonate.

Experimental

Samples were made by adding 100 ml. of a solution of potassium bromide to 1–20 g. each of mercuric oxide, mercurous bromide and mercury, in well-stoppered pyrex Erlenmeyer flasks. Some flasks had ground glass stoppers and some were stoppered with thoroughly cleaned rubber stoppers. No differences occurred which could be attributed to the stoppers. The flasks were agitated in a thermostat kept at 25.00 ± 0.02°. At intervals

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[3] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 487.

[4] (a) Bronsted, Z. *physik. Chem.*, *65*, *84*, 744 (1909), and (b) Ming Chow, THIS JOURNAL, 42, 488 (1920).

[5] Gerke and Geddes, J. Phys. *Chem.*, 31, 886 (1927).

of from twenty-four to seventy-two hours the suspended solids were allowed to settle, samples were pipetted off from the clear supernatant liquid and the flasks were reagitated. The weight ratio of mercuric oxide to mercurous bromide in the samples varied from 8:1 to 1:4.

The hydroxide concentration was determined by titration with standard sulfuric acid, using phenolphthalein as indicator. The bromide concentration was determined by adding an excess of silver nitrate solution and back titrating with standard thiocyanate solution, according to Volhard's method.

In most of the samples a solution of 0.088 or 0.099 N potassium bromide with no potassium hydroxide was used in making up the mixtures. In two of the mixtures a solution of potassium hydroxide and potassium bromide having approximately twice the equilibrium concentration of hydroxide was added to the mixture of mercuric oxide, mercurous bromide and mercury. In these cases just a trace of mercurous bromide had been added, and the hydroxide concentration of the solutions remained high; but upon adding 1 g. of mercurous bromide and agitating the solutions, the hydroxide concentration decreased to about the same value as that of the other samples.

The concentration ratios of hydroxide to bromide were first calculated and the activity ratios were then found by multiplying the concentration ratios by the ratio of the activity coefficients of the hydroxide and bromide ions in solutions of the same total ionic strength.[6] Our weighted mean activity ratio at equilibrium is 0.204, which is the equilibrium constant for the reaction

$$^1/_2\,\mathrm{HgO(s)} + {}^1/_2\,\mathrm{Hg(l)} + {}^1/_2\,\mathrm{H_2O(l)} + \mathrm{Br^-} = {}^1/_2\,\mathrm{Hg_2Br_2(s)} + \mathrm{OH^-} \qquad (1)$$

Substituting in the equation $\Delta F^\circ_{298} = -1365 \log K$, we obtain for the above reaction, $\Delta F^\circ_{298} = 943$ calories.

Brönsted[4a] found for the cell Hg, HgO(s), OH–, H_2, Pt: $E^\circ = -0.9268$ volt, which, converted to the new international volt, is -0.9265 volt. Ming Chow[4b] and also Buehrer (in an unpublished investigation) have found $E^\circ = -0.9264$ volt, from which we find, for the reaction

$$^1/_2\,\mathrm{Hg(s)} + {}^1/_2\,\mathrm{H_2O(l)} = {}^1/_2\,\mathrm{HgO(s)} + {}^1/_2\,\mathrm{H_2} \qquad (2)$$

$\Delta F^\circ_{298} = 21{,}375$ calories.

Gerke and Geddes[5] found for the cell H_2, H^+, Br^-, $Hg_2Br_2(s)$, Hg(l) $E^\circ = 0.1396$ volt, from which we obtain for the reaction

$$^1/_2\,\mathrm{H_2} + {}^1/_2\,\mathrm{Hg_2Br_2(s)} = \mathrm{H^+} + \mathrm{Br^-} + \mathrm{Hg(l)} \qquad (3)$$

$\Delta F^\circ_{298} = -3221$ calories.

Adding Equations 1, 2 and 3, and adding the free energy changes, we find

$$\mathrm{H_2O(l)} = \mathrm{H^+} + \mathrm{OH^-};\quad \Delta F^\circ_{298} = 19{,}097 \text{ calories}$$

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[6] Lewis and Randall, Ref. 3, p. 382.

Substituting this value in the expression $\Delta F^{\circ}_{298} = -1365 \log K$, we find $K_w = 1.02 \times 10^{-14}$ at 25°, as compared to 1.005×10^{-14} by Lewis and Randall, and 1.04×10^{-14} by Kohlrausch and Heydweiller.

TABLE I

COMPOSITION OF SOLUTIONS IN EQUILIBRIUM WITH MERCURIC OXIDE AND MERCUROUS BROMIDE

Weight ratio HgO/Hg_2Br_2	Time of shaking, hours	Concn of hydroxide. mole/liter	Concn. of bromide mole/liter	Concn. ratio	Activity ratio
1:4	0	.....	. .	0	0
	81	0.01297	0 0710	0.1827	0.187
	170	.01316	.0693	.1899	.195
1:2	0	. . .	. . .	.190	...
	23	,01412	.0710	.1989	.203
	70	.01305	.0682	.1913	.196
	132	.01283	.0654	.1962	.200
1:1	0	.....	.....	0	0
	26	,01402	.06975	.2010	.206
	146	,01392	.0698	.1994	.204
	298	.01370	.0689	.1988	.204
1:1	0	.....	. . .	.19	...
	23	.00904	.0467	.1936	.197
	70	,00901	.04605	.1956	.199
	132	.00891	.0450	.1980	.202
1:1	0	.....	. . .	.18	...
	24	.01384	.0704	.1966	.202
	80	.01383	.0703	.1967	.202
	136	.01343	.0705	.1905	.196
2:1	0	.....	.....	0	0
	26	.01415	.0703	.2013	.206
	142	.01389	.0699	.1987	.204
	226	.01363	.0700	.1947	200
	340	.01353	.0699	.1935	.199
2:1	0	.....	.....	.24	. .
	38	.01873	.09025	.2075	.213
	86	.01836	.08995	.2041	.209
	143	.01735	.0902	.1923	.197
2:1	0	.....	.....	ca0.4	...
	189	.02019	.0924	.2185	.223
	249	.01926	.0911	.2114	.216
6:1	0	.....	.....	ca0.4	...
	123	.01856	.09065	.2047	.210
	214	.01903	.0895	.2126	.218
	274	.01817	.0896	.2028	.208
8:1	0	.....	.....	0	0
	72	.01316	.0647	.2034	.209
	118	.01325	.0645	.2054	.211
				Mean activity ratio	.204

T. Fischer and H. von Wartenberg[7] report evidence of compound formation between HgO and Hg_2Br_2 in contact with water at 180°. The fact that under our experimental conditions the hydroxide–bromide ratio was independent of large changes in the mercuric oxide–mercurous bromide ratio indicates that we were obtaining the equilibrium with respect to the mercuric oxide and mercurous bromide, and not with respect to some compound of the two.

About three months after the experimental work had been completed, a new solid phase was observed in some of our mixtures. It is purplish-red and can very readily be distinguished from the mercuric oxide present. The compound has appeared in only a few of our samples. The formation of the compound is well illustrated by sample Number 4, which was made up April 4, 1928. Within twenty-four hours the hydroxide–bromide ratio became 0.20 and remained there for five days or more. During the following September the formation of the new compound was observed. By May, 1929, no mercurous bromide was visible in the mixture, and the hydroxide-bromide ratio had risen to 0.34. Solutions in equilibrium with mercuric oxide and the compound will undoubtedly show a higher hydroxide–bromide ratio than those in equilibrium with mercuric oxide and mercurous bromide, or those in equilibrium with the compound and mercurous bromide. The measurement of the two equilibria with the compound would serve as a valuable check on our measurements with mercuric oxide and mercurous bromide, but thus far we have been unable to prepare sufficient of the compound to carry out such measurements, nor to obtain it in sufficiently pure state to establish its composition.

Summary

The equilibrium constant for the reaction

$$^1/_2\,HgO(s) + {}^1/_2\,Hg(l) + {}^1/_2\,H_2O(l) + Br^- = {}^1/_2\,Hg_2Br_2(s) + OH^-$$

has been measured, and found to be 0.204 at 25°.

The dissociation constant of water at 25° has been calculated from the above equilibrium constant and the electrode potentials of the mercury–mercurous bromide–bromide ion electrode, and of the mercury–mercuric oxide–hydroxide ion electrode, reported by other authors. The dissociation constant is found to be 1.02×10^{-14} as compared to 1.04×10^{-14} by Kohlrausch and Heydweiller, and 1.005×10^{-14} by Lewis and Randall.

The occurrence of compound formation between mercuric oxide and mercurous bromide, reported by Fischer and von Wartenberg, has been confirmed. The composition and chemical properties of the compound have not as yet been studied.

LAFAYETTE, INDIANA

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[7] Mellor, "A Comprehensive Treatise of Inorganic and Theoretical Chemistry," **1923**, Vol. **IV**, p. 876; *Chem.-Ztg.*, **29**, **308** (1905).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ROESSLER AND HASSLACHER CHEMICAL COMPANY]

EQUILIBRIUM IN THE SYNTHESIS AND DECOMPOSITION OF METHANOL

BY B. S. LACY, R. G. DUNNING AND H. H. STORCH

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Introduction

Attempts to obtain values of equilibrium constants for the reaction

$$2H_2 + CO = CH_3OH \qquad (I)$$

have been made in three ways, *viz.:* calculations based on measurements of equilibria in the two reactions

$$2H_2 + HCOOCH_3 = 2CH_3OH \qquad (II)$$
$$CH_3OH + CO = HCOOCH_3 \qquad (III)$$

calculations based on measurements of the specific heat of methanol down to liquid hydrogen temperatures and the third law of thermodynamics and, finally, direct experimental measurement of the equilibrium concentrations of the three gases. The first method was employed by Christiansen.[1] His measurements were admittedly of a preliminary character. Additional measurements of equilibria in Reactions II and III have been made by one of the authors and will be presented in this paper. The second method has been employed by Kelley[2,3] and by Smith,[4] their calculations being based on the specific heat data of Parks[5] and Kelley.[6] The third method may be subdivided into two types of experiments, *viz.:* those in which the measurement of equilibrium is made from the synthesis side only, the primary object being to test catalysts for their activity, and those in which measurements from both the synthesis and decomposition sides are made, the primary object being to obtain reliable equilibrium data.

In the first subdivision of the third method may be grouped experiments and calculations of Audibert and Raineau,[7] Lewis and Frolich,[8] Brown and Galloway[9] and Fieldner and Brown.[10] In the second subdivision should be placed the experimental work of Smith and Branting,[11]

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[1] Christiansen, J. *Chem. Soc.*, 413 (1926).
[2] Kelley, *Ind. Eng. Chem.*, **18**, 78 (1926).
[3] Kelley, *ibid.*, 21, 353 (1929).
[4] Smith, *ibid.*, 19, 801 (1927).
[5] Parks, THIS JOURNAL, 47,338 (1925).
[6] Kelley, *ibid.*, 51, 180 (1929).
[7] Audibert and Raineau, *Ind. Eng. Chem.*, 20, 1105 (1928).
[8] Lewis and Frolich, *ibid.*, 20, 285 (1928).
[9] Brown and Galloway, *ibid.*, 20, 960 (1928).
[10] Fieldner and Brown, *ibid.*, 20, 1110 (1928).
[11] Smith and Branting, THIS JOURNAL, 51, 129 (1929).

Newitt, Byrne and Strong[12] and the data to be presented below on the direct measurement of equilibrium in Reaction I.

The results obtained by the first and third methods of estimating the equilibrium constants of Reaction I are of the same order of magnitude (they agree within a factor of about 3). These results are, however, 10 to 50 times smaller than the lowest values obtained by the second method, i. e., by way of the specific heat data on methanol and the third law of thermodynamics. This discrepancy has thus far not been explained.[12a] In view of the recent determination of the entropy of methanol by Kelley,[6] whose value checks the earlier determination by Parks,[5] attention should be focused on other possible sources of error, such as a constant error in determining the entropy of methanol, or errors in the estimation of the entropies of hydrogen and oxygen.

The results presented in this paper were completed about eighteen months before the appearance of Smith and Branting's[11] paper. Although the authors' work does not furnish any clue to the source of the discrepancy mentioned above, the data furnish more reliable figures on equilibrium Reactions II and III, as well as additional confirmatory data on Reaction I. The experiments of Smith and Branting[11] were made at atmospheric pressure and at about 300°. The quantities of methanol in the equilibrium mixture at atmospheric pressure were very minute, necessitating sensitive colorimetric tests. The data of Newitt, Byrne and Strong[12] were obtained at 100 and at 70 atmospheres' pressure, the temperatures ranging from 280 to 338°. The quantities of methanol under these conditions were sufficient to permit the preparation of an easily identified derivative of methanol. The authors' measurements were made at 50 and at 20 atmospheres' pressure and at temperatures of 200, 250 and 300°. The amounts of methanol obtained from the equilibrium mixtures under these conditions were considerably larger than those of Newitt, Byrne and Strong, and were sufficient to permit qualitative and quantitative analysis (the latter involving fractional distillations). Due to the pressure of other work, it was not possible to make the measurements as complete or over as extended a range as could have been desired.

Calculations **Via** the Methyl **Formate** Reactions.—In some unpublished work done in 1922 by one of us, the equilibria of Reactions II and III were measured. Christiansen[1] also measured these at a later date. The experimentally determined constants of both observers are given in Tables I and II. Both authors used reduced copper as *a* catalyst for

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[12] Newitt, Byrne and Strong, *Proc. Roy. Soc. London,* **123A,** 236 *(1929).*

[12a] Since this was written, an article has appeared [Barnett F. Dodge, Ind. *Eng. Chem.,* **22,** 89 (1930)] in which it is argued that inaccuracy in the usually accepted value for the heat of formation of methanol may cause an error in the thermodynamically calculated K_p sufficient to account for the discrepancy.

studying Reaction II, and the analytical methods used by Lacy were essentially the same as those given by Christiansen, except that Lacy used a condenser at −80° which preceded two water and two sodium hydroxide scrubbers. In studying Reaction III Christiansen used a dynamic method with sodium methylate as a catalyst, whereas Lacy used a static method (autoclave plus pressure gage) with dissolved sodium methylate as a catalyst. Lacy started his experiments on Reaction III with mixtures containing 2 moles of $HCOOCH_3$, 8 moles of CH_3OH and 1 mole of CH_3ONa.

TABLE I

EQUILIBRIUM IN THE REACTION $2H_2 + HCOOCH_3 = 2CH_3OH$

$$K_p = \frac{(p_{HCOOCH_3})\ (p_{H_2})^2}{(p_{CH_3OH})^2}.$$

Temp, °C.	Kp	Observer	Temp., °C.	K_p	Observer
(A) Hydrogenation					
198.9	0.059	C	197.6	0.068	C
199.6	.060	C	225	.148	C
198.7	.058	C	183.4	.041	C
224.8	.103	C	192.2	.056	C
227	.144	C	208.3	,090	C
			180	.030	L
(B) Dehydrogenation					
209	0.086	C	198.9	0.035	C
214.2	.105	C	200	.029	C
189.4	.048	C	200	.056	L
195.3	.050	C	200[a]	.052	L
231.2	.140	C	250	.018	L

[a] This second experiment at 200° was done at about one-third the space velocity of the previous determination.

TABLE II

EQUILIBRIUM IN THE REACTION $CH_3OH + CO = HCOOCH_3$

$$K_p' = \frac{(p_{CH_3OH})\ (p_{CO})}{(p_{HCOOCH_3})}$$

(A) Synthesis of $HCOOCH_3$

Temp., °C.	K_p'	Observer
74	9.7	C
70	16.0	L

(B) Decomposition of $HCOOCH_3$

Temp., °C.	K_p	Observer	Temp., °C.	K_p	Observer
70	5.5	C	70	25	L
74	7 2	C	50	8.1	L
102	2 2	C	30	2.3	L
100	76	L			

The data of Tables I and II are plotted in Figs. 1 and 2, respectively, the common logarithm of the equilibrium constant being plotted against the reciprocal of the absolute temperature. Assuming that the slope of these curves remains constant up to 300°, we have for Reaction II the equation

$$\log K = -\frac{3149}{T} + 5.43 \qquad \text{(IV)}$$

and for Reaction III

$$\log K' = -\frac{1835}{T} + 6.6 \qquad (V)$$

In constructing Fig. 2, the curve as given favors Lacy's data rather than Christiansen's, for the latter are admittedly uncertain. Addition of Equations IV and V gives an equation for the equilibrium constant of Reaction I

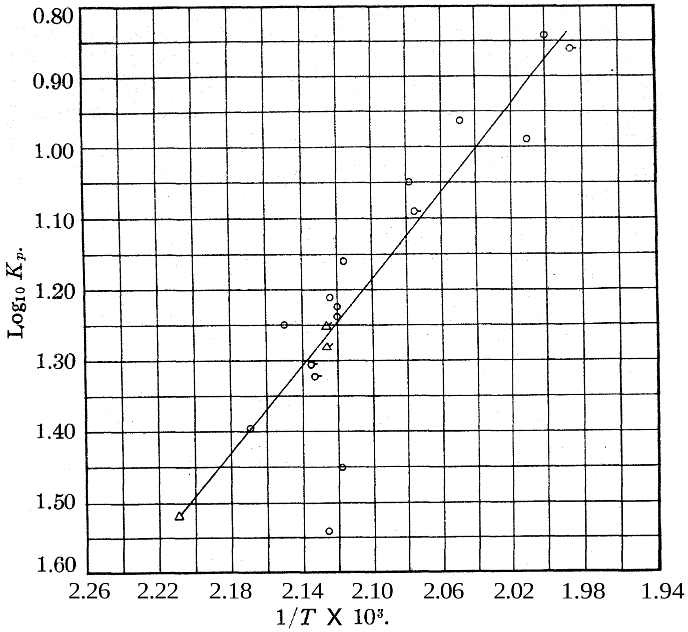

Fig. 1.—Reaction $2H_2 + HCOOCH_3 = 2CH_3OH$. O, Hydrogenation, Christiansen; A, hydrogenation, Lacy. O–, Dehydrogenation, Christiansen; A–, dehydrogenation, Lacy.

$$\log K'' = -\frac{4984}{T} + 12.04 \qquad (VI)$$

This formula yields the following equilibrium constants

Temp., °C.	200	250	300
$K''' = 1/K'' = (p_{CH_3OH})/(p_{CO})(p_{H_2})^2$	3×10^{-2}	3×10^{-3}	5×10^{-4}

These constants are of the same order of magnitude as those obtained by direct measurement (see Table VI).

Direct Measurement of Equilibrium in Reaction $2H_2 + CO = CH_3OH$

Description of Apparatus and Procedure.—The accompanying sketch illustrates the arrangement of the apparatus for the measurement of equilibrium from the decomposition side of Reaction I. Methanol was vaporized in a brass bomb (V) which was maintained at a constant temperature by the electric furnace (F) and the thermoregulator (R); 350 cc. of methanol was placed in the bomb, whose initial volume was 500 cc. The vapor pressure of the methanol was measured by a calibrated Bourdon gage.

A copper tube projecting from the bottom of the bomb into the vapor space was connected to the nipple (U). Through the tube and nipple the methanol vapor passed into the copper-lined bomb (B) containing the catalyst. The bomb was also maintained at a constant temperature by an electric furnace and a thermoregulator.

The off-gases passed through a copper tube to the pressure condenser (C). Methanol vapor was liquefied at this point and drawn off at the valve (X), while the non-condensable gases passed through the flowmeter (G) to the wetmeter (M). The space velocity of the gas was controlled by the valve (D) and was continuously indicated by the flowmeter.

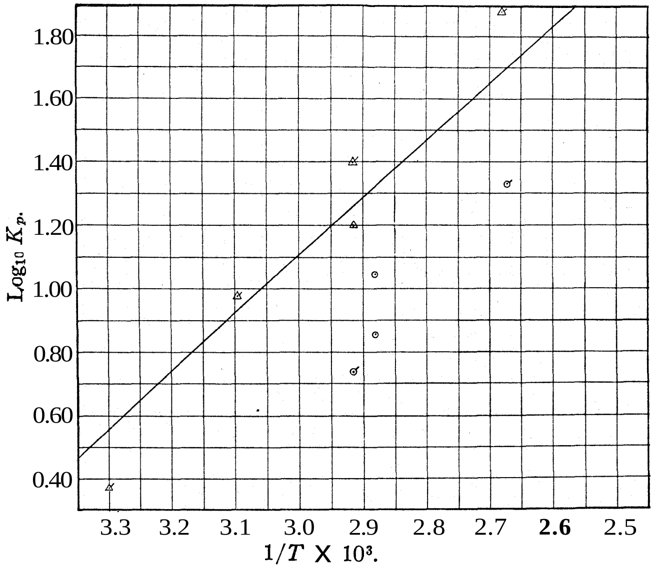

Fig. 2.—Reaction $CH_3OH + CO = HCOOCH_3$. ⊙, Christiansen, synthesis; A, Lacy, synthesis; ⊙–, decomposition; A–, decomposition.

For measurement of equilibrium in Reaction (I) from the synthesis side, the upper furnace and bomb were removed. Water gas which had been scrubbed with sodium hydroxide solution, then mixed with steam and passed over a water-gas shift catalyst at 450–500° and finally scrubbed again with sodium hydroxide solution, was compressed to the desired pressure, passed over activated carbon to remove any catalyst poisons and admitted to the catalyst chamber through the nipple (U).

Temperatures were measured by calibrated chromelalumel thermocouples imbedded in the walls of the bombs. During a number of experiments on the synthesis side of Reaction I, an additional couple was imbedded in the catalyst itself. This consisted of a copper tube through which an insulated constantan wire had been thrust. The end of the tube was welded over the end of the constantan wire, forming the hot junction of a copper-constantan couple which was capable of withstanding several hundred atmospheres pressure and which exposed only copper to the reactants. No difference in temperature was observed between this internal couple and the external one in the wall of the bomb. The maximum error in reading the couples is estimated as ±2°.

During two experiments the off-gases were scrubbed in two bead towers containing water in order to determine the loss of methanol in the off-gases. The maximum error involved in neglecting this is less than 0.3%.

A few synthesis experiments were made at twenty atmospheres using the same type of apparatus with the exception of the condenser. The vapors and off-gases were expanded through a small needle valve directly into a glass condenser cooled by carbon dioxide snow mixed with methanol, the temperature inside the condenser coil being held between −75 and −80°.

In all of the experiments the catalyst employed was a mixture of the oxides of copper, uranium and thorium, supported on asbestos. This catalyst was prepared as follows: 83 g. of $Cu(NO_3)_2 \cdot 3H_2O$, 10 g. of $UO_2(NO_3)_2 \cdot 6H_2O$ and 5 g. of $Th(NO_3)_4 \cdot 12H_2O$ were dissolved in 500 cc. of water. Fifty grams of acid-washed asbestos fiber was mixed with the solution, which was then heated to boiling and 100 grams of potassium hydroxide dissolved in 250 cc. of water was added. The mixture was then filtered, the filter cake being washed free from nitrates, and then dried at 150°. Before use the catalyst was reduced at 150–200° by passing a mixture of 90% of hydrogen and 10% of methanol over it for several hours, the methanol being employed to avoid any sudden rise in temperature due to the heat of reduction of copper oxide.

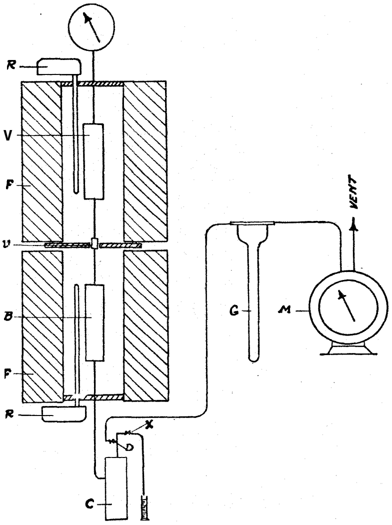

Fig. 3.—Apparatus for measuring equilibrium in the methanol reaction.

Results

Tables III, IV and V contain all of the essential data for the calculation of the equilibrium constants. Unless otherwise specified, the product was practically pure (above 95%) methanol, no correction being made for the small amounts of water, methyl formate and higher alcohols which were present. The method of calculation is as follows.

A = Off-gas in liters at 22° and 1 atmosphere

B = CH_3OH in liters at 22" and 1 atmosphere

C = $(A + B)$ = volume of equilibrium mixture calculated as at 22° and 1 atmosphere

D = $[(A + 3B) \times$ volume fraction of CO in entering gas $- B]$ = volume of CO in equilibrium mixture calculated at 22° and 1 atmosphere

E = $(A - D)$ = volume of H_2 in equilibrium mixture calculated at 22° and 1 atmosphere

P = total pressure

$$K_p = \frac{(p_{CH_3OH})}{(p_{CO})\,(p_{H_2})^2} = \frac{B \times C^2}{D \times E^2P^2}$$

The constant K_p was calculated using partial pressures as indicated above, no correction being made for the deviations of the gases from the laws of perfect gases, since so far as the pure substances H_2, CO and CH_3OH are concerned, such deviations are of the same order of magnitude as the experimental errors. The constants obtained by using fugacities are about 15% lower than those using pressures, whereas the average

TABLE III

EQUILIBRIUM DATA FOR SYNTHESIS OF METHANOL AT 50 ATMOSPHERES

Expt.	Off-gas, liters at 22° and 1 atm.	CH_3OH, cc. at 22°	CO in entering gases, %	Temp., °C.	S. V. H.	Conversion of CO to CH_3OH, %	K_p
7a	31.81	15.6	16.9	200	136	98.1	0.036
7b	35.74	17.6	16.9	200	48	98.3	,040
7c	28.67	14.1	16.9	200	90	98.3	.035
7d	28.16	46.4	27.5	200	63	88.0	.016
7e	31.72	53.8	27.5	200	75	91.2	.021
7f	35.71	10.2	16.6	250	83	69.4	.0014
7g	27.22	7.2	16.9	250	67	64.0	.0012
7h	35.32	9.4	18.1	250	75	60.0	.0010
8a	29.46	11.6	26.9	250	35	51.6	.0011
8b	30.90	12.8	27.5	250	35	52.0	.0011
8c	26.18	11.3	28.0	250	40	52.3	.0012
7i	74.29	6.2	19.3	300	90	22.7	.00019[b]
7j	77.54	6.0	19.3	300	60	21.3	.00017[b]
8d	52.75	4.8[a]	25.2	300	30	15.0	.00013
8e	42 61	3.9[a]	25.2	300	25	15.0	.00013
8f	33.28	2.6[a]	252	300	20	12.7	.00011
8g	48.40	3.6[a]	25.2	300	20	12.5	.00011

[a] This product was only 77% CH_3OH. In calculating the equilibrium constant the partial pressure of CH_3OH was taken as 77% of this pressure as ordinarily calculated, the partial pressures of CO and H_2 being calculated as indicated above (and hence no correction was made for the small amounts of CO and H_2 converted to products other than methanol).

[b] The average of these two values Nos. 7i and 7j, that is, (0.00019 + 0.00017)/2 = 0.00018, has been used in Table VI as the value for K_p at 300° from the synthesis measurements. The reason for picking out these values and discarding Nos. 8d, 8e, 8f and 8g is that the relatively low purity of the methanol produced in these last showed that, due to the much lower S. V. H., side reactions went onto a considerable extent, while in Nos. 7i and 7j this was not the case. Furthermore, since equilibrium is here being approached from the synthesis side, all observed values of K_p must necessarily be lower than the true value, consequently the higher figures represented by 7i and 7j should be nearer the true value of K_p.

TABLE IV

EQUILIBRIUM DATA FOR DECOMPOSITION OF METHANOL AT 50 ATMOSPHERES

Expt.	Off-gas, liters at 22° and 1 atm.	CH_3OH, cc. at 22°	Temp., °C.	S. V. H.	Decomposition, %	K_p
5a	26.54	11.6	250	90	55.8	0.0011
5b	32.54	17.2	250	85	50.0	.0015
5c	40.89	18.2	250	40	55.0	.0012
6a	28.66	3.0	300	90	84.0	.00019
6b	51.02	5.6	300	90	83.4	.00020
6c	32.21	3.3	300	55	84.3	.00019
6d	67.41	7.1	300	70	84.0	.00020

TABLE V

EQUILIBRIUM DATA FOR SYNTHESIS OF METHANOL AT 20 ATMOSPHERES

Expt.	Off-gas. liters at 22 °C. and 1 atm.	CH_3OH, cc. at 22°	Temp., °C.	CO in entering gas, %	S. V. H.	Conversion of CO to CH_3OH, %	K_p
3a	105.84	13.4	250	19.8	43	31.5	0.0019
3b	122.25	15.0	250	19.8	45	30.8	.0019
3c	96.22	11.0	250	19.8	27	28.9	.0017
3d	143.16	15.8	250	19.8	25	28.1	.0016

deviation from the mean of the pressure constants for the experiments at 50 atmospheres was **30%** at ZOO°, 9% at 250° and 8% at 300°.

The space velocity per hour of the reactants (which will hereafter be designated as S. V. H.) was calculated as at one atmosphere and 22°. Hence in order to obtain the true S. V. H. inside the bomb, it is necessary to multiply by $T/(P \times 295)$, where T is the absolute temperature and P is the total pressure.

Discussion

Table VI contains the averages of the results of Tables III, IV and V, as well as the constants calculated for Reaction I via the methyl formate equilibria. This table also includes constants calculated by Kelley[2,3] and by Smith,[4] their equations being based on the use of the specific heat data of Parks[6] and of Kelley.[6] The experimental results of Smith and Branting[11] and of Newitt, Byrne and Strong,[12] and the results of calculations using the Nernst approximation formula are also included in Table VI.

TABLE VI

COMPARISON OF EQUILIBRIUM CONSTANTS OBTAINED BY VARIOUS METHODS

				Temperature, °C.				
No.	Method	Pressure, atm.	Reference	200 K_p X 10^2	Z50 K_p X 10^3		300 K_p X 104	
1	Direct meas., synth. and decomp.	65–100	12	4.8"	2.1"		1.6	
2	Dir. meas., synth.	50	Authors	3.0	1 2	Av.,	1.8	Av.,
2a	Dir. meas., decomp.	50	Authors	. . .	1.3	1.25	1.95	1.9
3	Dir. meas., synth.	20	Authors	.	1 8		. . .	
4	Dir. meas., synth.	1	11	. . .	. .		6.5	
4a	Dir. meas., decomp.	1	11	. . .	. . .		6.6	
5	Via $HCOOCH_3$ reactions	1	Lacy, 1	3	3		5	
5a	Via $HCOOCH_3$ reactions	1	1	5	6		8	
6	Via third law calcd.	. .	3	121	80		87	
7	Via Nernst approx.	. . .	Authors	8	4		4	

[a] By extrapolation of measurements at higher temperature.

The values of No. 1 of Table VI are those tabulated by Newitt, Byrne and Strong,[12] being derived from the general expression which they give to represent the results of all their measurements over the range 280–338°, namely

$$A F = 70.5T - 30{,}500$$

which corresponds to

$$\log_{10} K_p = -15.42 + \frac{6672}{T}$$

The values of Nos. 4 and 4a were calculated from the results obtained by Smith and Branting[11] at 304°.

The Nernst approximation formula used to derive the data given in Table VI is

$$\log K = \frac{24{,}750}{4.58T} - 3.5 \log T - 3.2 \qquad \text{(VII)}$$

The chemical constants used in deriving Equation VII are: $H_2 = 1.6$, $CO = 3.5$, $CH_3OH = 3.5$, which correspond to the original conventional constants of Nernst.

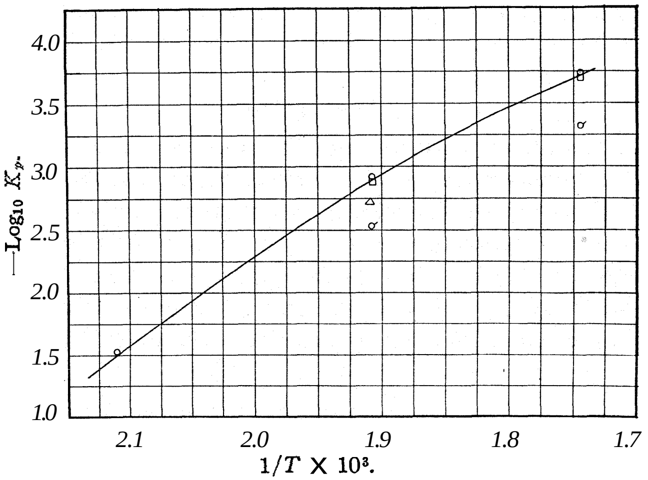

Fig. 4.—O, Synthesis at 50 atm.; A, synthesis at 20 atm.; □, decomposition at 50 atm.: Lacy, Dunning and Storch; O-, via methyl formate reaction, Lacy and Christiansen.

The average values of Tables III, IV and V, *i. e.*, the values of Nos. 2, 2a and 3 of Table VI are plotted in Fig. 4, along with the data obtained from Lacy's and Christiansen's work. The slope of the curve gives for the heat of Reaction I, in the temperature range 200–300°, the value 24,000 calories. This is in fair agreement with the equation

$$AH = -21{,}300 - 14.0T + 0.00825T^2 \qquad \text{(VIII)}$$

which is used by Kelley[2] and is based upon the following specific heat equations

$$\text{Hz}, C_p = 6.65 + 0.0007T \qquad \text{(IX)}$$
$$CO, C_p = 6.84 + 0.00038T \qquad \text{(X)}$$
$$CH_3OH_{(gas)}, C_p = 6.16 + 0.0183T$$

and upon the following heat of formation of methanol

$$H_{(298)} \text{ for } 2H_2 + CO = CH_3OH_{(gas)} = -24{,}750 \text{ cal.} \qquad \text{(XII)}$$

Using Equation VIII and any point on the curve of Fig. 4, the following free energy equation for Reaction I is obtained

$$AF = -21{,}300 + 14.0T \ln T - 0.00825T^2 - 30.84T \qquad \text{(XIII)}$$

An inspection of Table VI indicates that, excepting the calculations by way of the third law of thermodynamics, the constants are of the same order of magnitude. The third law calculations yield constants the lowest of which are 10–50 times larger than those determined experimentally. This very large discrepancy can scarcely be due to any large error in the experimental determinations, in view of the fact that the several experimenters agree as to the order of magnitude, nor can the discrepancy be attributed to any experimental error in the measurement of the specific heat of methanol, in view of Kelley's[6] recent work.

It is, however, conceivable that some constant error such as may for example be due to a very slow rate of approach to equilibrium of two forms of methanol may be involved. The value for the entropy of hydrogen used by Kelley[3] in calculating the entropy change of Reaction I is in error by an appreciable amount due to such a constant error, *viz.*, the very slow rate of transformation of ortho to para hydrogen in the absence of a catalyst.[13,14]

It also appears desirable to review the experimental basis for the entropy of carbon monoxide, and to redetermine those values which involve a possible source of error.

The figure 1.6×10^{-4} obtained by Newitt, Byrne and Strong[12] for K_p at 300° agrees fairly well with the average value of the authors' constant for the same temperature (which rests on measurements made at 50 atm., *i. e.*, in the same pressure range), namely, 1.9×10^{-4}. (A difference in temperature of about 3° would account for this small difference in K_p). This value of K_p for 300°, however, differs quite considerably from Smith and Branting's average value of 6.5×10^{-4}, which rests on measurements made at atmospheric pressure.

This 4:1 discrepancy cannot be due to errors introduced by the use of pressures instead of fugacities,[15] for such errors would decrease by about 15% the constants obtained by the authors and by Newitt, Byrne and Strong, thus increasing the difference between these results and those of Smith and Branting. Two other possible explanations of this discrepancy are: first, the possibility of solvent effects in the gas mixture causing the fugacities of the constituents to be different from what they would be in an ideal solution; second, experimental errors.

Smith and Branting's equilibrium determinations at atmospheric pressure can hardly be in error due to solvent effects, since these are usually

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[13] Bonhoeffer and Harteck, *Z. physik. Chem.*, **4B**, 113 (1929).

[14] Rodebush, *Proc. Nat. Acad. Sci.*, **15**, 678 (1929).

[15] For pressure–fugacity relations, see Fig. 4 of Smith and Branting's article.

negligible at atmospheric pressure.[16] If the solvent effect which was calculated for ethylene–argon mixtures under pressure at 25° by Gibson and Sosnick[16] also exists in mixtures of methanol, hydrogen and carbon monoxide, then it is quite possible that the equilibrium constants obtained at 50–70 atmospheres may be in error by a few per cent. Whether this error would make the constants obtained at 50-70 atmospheres larger or smaller than those obtained at one atmosphere is uncertain, but it seems unlikely (although not impossible) that the solvent effect will explain a discrepancy as large as 300–400% such as exists between the determinations made at 50–70 atmospheres pressure and those made at one atmosphere, for deviations from the laws of perfect solutions of sufficient magnitude to account for such large errors have never been reported. In fact, in the closely parallel case of nitrogen and ammonia, studied by Lurie and Gillespie[17] for a temperature of 45° and total pressures of 7 to 60 atmospheres, the data indicate no deviation whatever from the laws of ideal solutions. Similarly in the work of Larson and Dodge[18] on equilibrium in mixtures of nitrogen, hydrogen and ammonia, the differences between the constants obtained at 50 atmospheres and at one atmosphere are practically negligible, being about 2% at 500°, 6% at 450°, 1% at 400°, 3% at 375° and 6% at 350°. These differences are so small and irregular that experimental error will probably account for them.

It seems more probable that the discrepancy between the constants obtained at one atmosphere and those obtained at 50–70 atmospheres is due to experimental errors. The fact that the two entirely distinct series of high pressure equilibrium determinations, one made by Newitt, Byrne and Strong and the other by the authors, give closely concordant results, makes any serious experimental error in the value of the constant for 300° and 50–70 atmospheres seem highly improbable. Concerning the possibility of experimental error in Smith and Branting's measurements at one atmosphere, despite the great care which they exercised in establishing the validity of their analytical methods and data, the fact must be considered that difficulties of experimental technique in any determination at one atmosphere are very great. Thus while in the authors' work at 50 atmospheres the methanol constituted about one-tenth of the equilibrium mixture, and the amounts of methanol separated were of the order of 5 to 20 g. (thus permitting fractional distillation, boiling point and density determinations), in Smith and Branting's work the methanol made up only 1/10,000 of the equilibrium mixture, and the amount of methanol (estimated colorimetrically) apparently obtained in a week's run was only about 0.003 g. The possibility of serious error in estimating

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[16] Gibson and Sosnick, THIS JOURNAL, 49,2172 (1927).

[17] Lurie and Gillespie, ibid., 49, 1146 (1927).

[18] Larson and Dodge, *ibid.*, 45,2918 (1923).

such minute quantities of methanol is apparent if one considers the chance of the presence in the catalyst or in the original CO + H_2 mixture of a minute amount of some volatile organic impurity not decomposable by the catalyst and reacting like methanol in colorimetric tests. Smith and Branting do not state whether blank tests to eliminate such possibilities were made, for example, blank tests consisting of passing the CO + H_2 mixture through a reaction vessel not containing any catalyst, and of passing hydrogen alone through the catalyst.

Summing up the conclusions as to this 4:1 discrepancy: the explanation consists either in experimental error in the determination at one atmosphere, or in the value of the constant for 50–70 atmospheres being, in fact, only about one-fourth of the value of the constant for one atmosphere as a result of a very large solvent effect (according to which the fugacities of methanol, and perhaps also those of hydrogen and of carbon monoxide or of all three, in mixtures of these at 50-70 atmospheres deviate enormously from the fugacities of these constituents in the pure state. In fact, the pressure range might be given as 20-70 atmospheres, in which the constants are only about one-fourth of those at one atmosphere, in view of the fair agreement between the synthesis figures at 20 atmospheres and the 50 atmospheres pressure data summarized in Table VI.

In view of the above considerations, it appears very desirable to carry on further determinations at one atmosphere, and to extend the range of the equilibrium determinations to pressures of 5, 10 and 20 atmospheres. Such additional experimental data would not only furnish information concerning the variation of the equilibrium constant with pressure, but would also present additional evidence as to whether the deviations of gaseous mixtures from the laws of perfect solutions can really be large enough to account for a 4:1 variation in equilibrium constants in so moderate a range of pressure as 1 to 50 atmospheres.

For 250° it will be noted that the value for K_p obtained by the authors in direct measurements at this temperature (at 50 atm.), namely, 1.25×10^{-3}, differs appreciably from the value of 2.1×10^{-3} which is calculated by Newitt, Byrne and Strong by extrapolation of their. measurements made between 280 and 338" at pressures of 65 to 100 atmospheres.

Summary

The equilibrium constants for the reaction $2H_2 + CO = CH_3OH$ were measured from both the synthesis and decomposition sides at 250 and 300°, and also at 200° from the synthesis side only, using in all cases 50 atmospheres total pressure. Some measurements were also made from the synthesis side at 250° using 20 atmospheres total pressure.

These equilibrium constants were also calculated from measurements of equilibria in the two reactions.

$$2H_2 + HCOOCH_3 = 2CH_3OH$$
$$CH_3OH + CO = HCOOCH_3$$

Both sets of constants are of the same order of magnitude (they agree within a factor of about three), but the lowest figures obtained by calculations based on the use of specific heat data, and the estimated entropies of hydrogen and oxygen, are about 10–50 times as large as those obtained experimentally. The existence of a large discrepancy here, which was mentioned by Smith and Branting, is thus confirmed.

The data obtained by the authors at 300° and 50 atmospheres pressure agree very well with those obtained at 70 atmospheres by Newitt, Byrne and Strong, but are only about three-tenths as large as those obtained by Smith and Branting at atmospheric pressure. A discussion of possible explanations of this discrepancy is presented.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGY, HARVARD SCHOOL OF PUBLIC HEALTH]

THE NEPHELOMETRIC ANALYSIS OF ZINC

BY LAWRENCE T. FAIRHALL AND JOHN R. RICHARDSON

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In plant and animal tissues certain elements occur in amounts that are too small for accurate determination by the usual methods of quantitative analysis and yet comparatively gross for application of the methods of microchemistry. Zinc, which is one of these elements, is apparently important to animal life. Its wide distribution in food—particularly its concentration in the germ elements, such as the endosperm of grain and yolk of egg—points to a possible need. Furthermore, tissue zinc is susceptible to changes in condition which affect the salt metabolism in general[1] and which indicate some function as yet unknown in cellular processes.

Unfortunately, methods for the analysis of the small amounts of zinc that occur in animal tissues and fluids are difficult, and results approaching exactness are attained only with considerable skill and experience. This is owing not only to the fact that these traces of zinc are found in the presence of enormously greater quantities of other salts, but more particularly to the fact that zinc forms no useful colored salts, nor very insoluble compounds which sharply differentiate it from its milieu.

No simple, exact method for the gross estimation of zinc has yet been found in spite of the expenditure of considerable effort in this direction.[2] Methods for the analysis of *traces* of the metal are quite as unsatisfactory. Of the methods available for the analysis of amounts of zinc in the vicinity of

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[1] L. T. Fairhall, *J. Biol. Chem.*, 70, 495 (1926).

[2] F. R. Bichowsky, *J. Ind. Eng. Chem.*, 9,668 (1917).

a few milligrams or less, the nephelometric ferrocyanide method developed first by Mylius[3] is still apparently the most accurate, although it, too, is open to error. Not only the nephelometric determination itself, but the separation of zinc from other metals is difficult and subject to losses owing either to the frequently colloidal character of the compounds formed, or to their solubility in acids.

Iron frequently accompanies zinc and is (as in blood) much greater in amount. As a consequence it is a disturbing factor of some magnitude in the separation of zinc. It is possible to effect the separation of the two by precipitation of the iron with cupferron in acid solution,[4] but with very minute amounts of iron this has occasionally proved uncertain and in these cases has necessitated a new separation and analysis. Furthermore, it is tedious in application, as it requires destruction of the excess cupferron before the analysis is carried forward to completion.

For these reasons, an attempt was made to define more exactly the conditions under which traces of zinc could be separated and identified in the ash of biological material.

Experimental

An initial study of the effect of changes in acidity disclosed the fact that minute amounts of zinc could be recovered quantitatively as sulfide over a range of hydrogen-ion concentration at which iron is not similarly precipitated. For this purpose analysis was made of 100-cc. samples of solution each of which contained 1 mg. of zinc, 2 mg. of copper, 2 mg. of iron and 2 g. of sodium citrate. The solutions were adjusted to various degrees of acidity varying from a hydrogen-ion concentration of $C_{\mathrm{H}} = 10^{-3}$ to $C_{\mathrm{H}} = 10^{-6.6}$. The hydrogen-ion concentrations were measured electrometrically. The presence of copper is desirable in the precipitation of zinc as sulfide, when the latter metal is present in minute amount, in order to take advantage of the co-precipitation of the two. Furthermore, minute amounts of copper are usually present in animal tissues and must be removed in any event in the ordinary course of analysis.

The results obtained in this study are shown in Table I and in Fig. 1. These experiments indicated that with a hydrogen-ion concentration less than $10^{-4.5}$ iron becomes a factor of importance. On the other hand, at a hydrogen-ion concentration greater than $10^{-2.5}$ the recovery of zinc was poor. Over the range $C_{\mathrm{H}} = 10^{-2.5}$ to $C_{\mathrm{H}} = 10^{-4}$ both the recovery of zinc was good and the contamination due to iron was nil, so that there is a definite region between $C_{\mathrm{H}} = 10^{-2.5}$ and $C_{\mathrm{H}} = 10^{-4}$ at which minute amounts of zinc may be quantitatively separated from iron by precipitation as the sulfide.

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[3] **E. Mylius,** ***Z. anal. Chem.*****, 19, 101 (1880).**

[4] **L. T. Fairhall,** ***J. Ind. Hyg.*****, 8, 165 (1926).**

TABLE I

THE OPTIMUM RANGE OF ACIDITY FOR THE SEPARATION OF ZINC AND IRON AS SULFIDE

C_H	Zinc recovered, %	C_H	Zinc recovered, %	C_H	Iron recovered. %
$10^{-1.62}$	3	$10^{-3.35}$	101	$10^{-5.0}$	12.0
$10^{-1.78}$	11	$10^{-3.60}$	104	$10^{-5.2}$	15.7
$10^{-2.23}$	40	$10^{-3.90}$	100	$10^{-5.4}$	19.2
$10^{-2.44}$	80	$10^{-4.15}$	101	$10^{-5.6}$	36.7
$10^{-2.61}$	100	$10^{-4.49}$	Iron	$10^{-5.8}$	56.0
$10^{-2.72}$	99	$10^{-5.21}$	contaminated	$10^{-5.9}$	57.7
$10^{-2.89}$	102	$10^{-6.33}$	Iron	$10^{-6.0}$	68.2
$10^{-3.02}$	100		contaminated	$10^{-6.2}$	82.2
$10^{-3.12}$	99		Iron	$10^{-6.4}$	85.5
$10^{-3.27}$	98		contaminated	$10^{-6.6}$	91.0

Fales and Ware[5] found that in zinc analysis by the usual methods and using one-gram samples of zinc ammonium sulfate, the best range for zinc precipitation lies between a hydrogen-ion concentration of 10^{-2} and 10^{-3}.

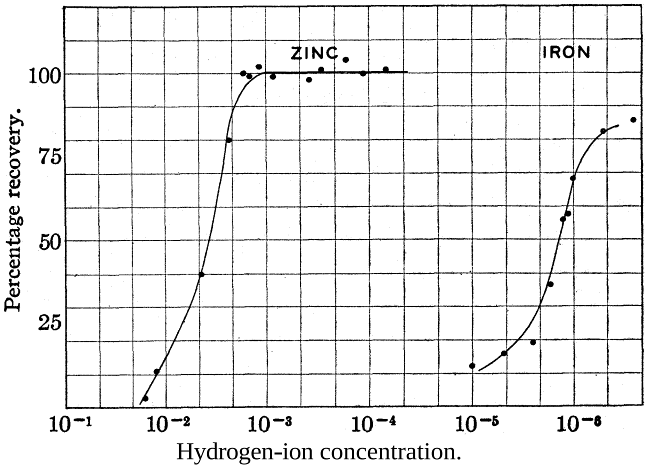

Fig. 1.

With concentrations greater than 10^{-2} precipitation is incomplete; with less than 10^{-3} the precipitate becomes slimy and difficult to filter. With minute quantities, however, losses are encountered when the hydrogen-ion concentration is greater than $10^{-2.5}$. A hydrogen-ion concentration of 10^{-3} is a convenient point of precipitation for these small amounts and may readily be adjusted by means of the two indicators thymol blue and brom chlor phenol blue. Sliminess or granularity of the zinc-copper sulfide precipitate is a factor of no consequence with minute quantities, as the filtration is always efficient.

Factors Influencing **the** Opalescence of Zinc **Ferrocyanide.**—Accuracy in estimating zinc nephelometrically as the ferrocyanide can be attained

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[5] H. A. Fales and G. M. Ware, THIS JOURNAL, 41, 487 (1919).

only by careful attention to several factors which markedly influence the degree of turbidity produced. Important among these are acidity, salt concentration and time. Very small variations in acidity produce surprisingly large changes in opacity for a given quantity of zinc. Thus a solution 1.53 X 10^{-5} molar with respect to zinc at an acidity of 0.002 N has an apparent zinc content of 7.65 × 10^{-5} if the acidity is increased to 0.028 *N*—or, in other words, the apparent zinc content is increased five-fold with a slight shift in acidity. Furthermore, the readings are subject to vagaries at the higher acid level and fluctuate more with slight differences in acid concentration than at the lower acid level. Quantities of zinc lower in amount (of the order 3 X 10^{-6} molar) do not respond to this degree of sensitivity to acid.

TABLE II

THE EFFECT OF ACIDITY UPON THE OPALESCENCE OF ZINC FERROCYANIDE

C_H	True concentration, moles X 10^5	Apparent concentration, moles X 10^5	C_H	True concentration, moles X 10^5	Apparent concentration, moles X 10^5
$10^{-2.49}$	1.53	1.53	$10^{-2.53}$	7.65	7.65
$10^{-2.42}$	1.53	1.53	$10^{-2.27}$	7.65	7.65
$10^{-2.26}$	1.53	1.53	$10^{-2.20}$	7.65	10.12
$10^{-1.93}$	1.53	2.76	$10^{-1.92}$	7.65	10.00
$10^{-1.68}$	1.53	3.98	$10^{-1.90}$	7.65	10.35
$10^{-1.41}$	1.53	4.50	$10^{-1.68}$	7.65	11.35
$10^{-1.03}$	1.53	7.67	$10^{-1.38}$	7.65	13.09
			$10^{-0.82}$	7.65	16.87

The effect of variation in degree of acidity upon the opalescence of zinc ferrocyanide is shown in Table II and in Fig. 2. The zinc concentrations in these two series were 1.53 X 10^{-5} and 7.65 × 10^{-5} molar, respectively, while the acid concentration was varied from a hydrogen-ion concentration

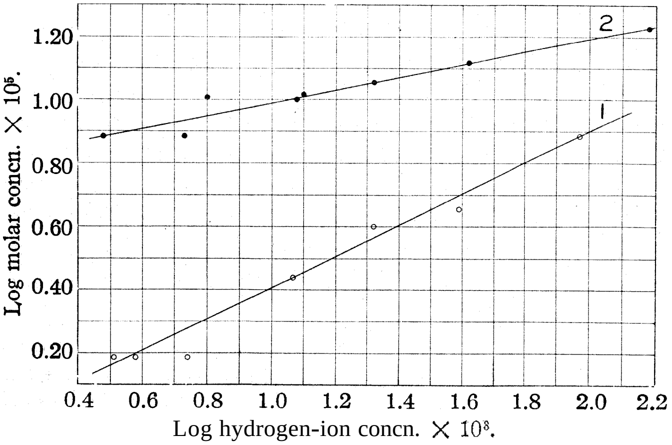

Fig. 2.

of $10^{-0.83}$ to $10^{-2.53}$. The apparent zinc content of each solution was determined nephelometrically against standards identical in all other respects, except that the acidity was maintained at a C_H of $10^{-2.53}$.

It is apparent from Fig. 2 that the change in opalescence with acidity takes the form $y = x^n k$, where y and x represent the degree of opalescence and hydrogen-ion concentration, respectively, and k is a constant. Decreasing the hydrogen-ion concentration to points lower than $10^{-2.50}$ affects the opalescence somewhat, but much less proportionately than at the higher acid level. Moreover, at the higher acid concentrations the Tyndall blue effect is not so apparent. A fixed hydrogen-ion concentration of $C_H = 10^{-2.3}$ was adopted as most satisfactory for the nephelometric determination of zinc as ferrocyanide.

Salt Concentration.—An excess of salt (in this case potassium chloride) is undesirable, for it not only increases the opacity of the suspension, but also causes the development of a yellowish tinge in the suspension which makes the readings difficult. In order to determine the degree of interference to which various amounts of potassium chloride will give rise, a series of experiments was made in which a constant amount of zinc in the presence of variable amounts of potassium chloride was determined nephelometrically against standards having a salt content of one gram of potassium chloride per liter of solution The acidity was the same throughout. These results are shown in Table III and in Fig. 3.

TABLE III

EFFECT OF SALT CONCENTRATION UPON THE OPALESCENCE OF ZINC FERROCYANIDE

True zinc concentration, 7.66×10^{-5} molar

Number	1	2	3	4	5	6	7	8	9
KCl, moles $\times 10^{-3}$	6.7	13.4	20.1	26.8	33.5	40.3	47.5	53.7	66.4
Apparent zinc concn., moles $\times 10^{-5}$	3.1	4.6	6.3	7.6	9.5	11.5	12.9	14.6	15.3

It will be observed that the apparent values obtained for **0.25** mg. of zinc ranged from **0.10** mg. to more than **0.50** mg. in proportion as the salt concentration varied. It was quite apparent (especially at high salt concentrations) that the increased opacity was accompanied by larger flocculates, so that while the degree of dispersion was decreased the opacity was of quite a different type from normal and therefore increased the difficulty of making satisfactory readings.

The apparent zinc content varied directly as the salt concentration. As a result of these experiments and as a convenient amount to use in the ordinary course of analysis, the quantity of salt was so adjusted that the opalescence was uniformly developed in a solution **0.0268** molar with respect to potassium chloride.

Time.—Time is always a factor of importance in the development of opalescence. After the addition of potassium ferrocyanide to a very dilute solution of a salt of zinc, the resulting solution becomes a dispersed, unstable system. Coalescence is determined by the collision and adhesion of the dispersed particles. With zinc ferrocyanide several minutes are necessary for the attainment of maximum opalescence. The time necessary to reach this point was determined with amounts of zinc varying from 0.1 mg. to 0.4 mg. in 50 cc. of solution and was found to vary from three and one-half minutes for the lower concentration to six minutes for the upper. Maximum opalescence is certainly attained by the end of ten minutes over this range and persists at a maximum for fully twenty minutes longer. The turbidity is affected by decomposition of the ferrocyanide to some extent on exposure of the solution to direct sunlight for half an hour or more, so that it is advisable to carry out the determinations in somewhat subdued daylight. Artificial illumination is generally unsatisfactory.

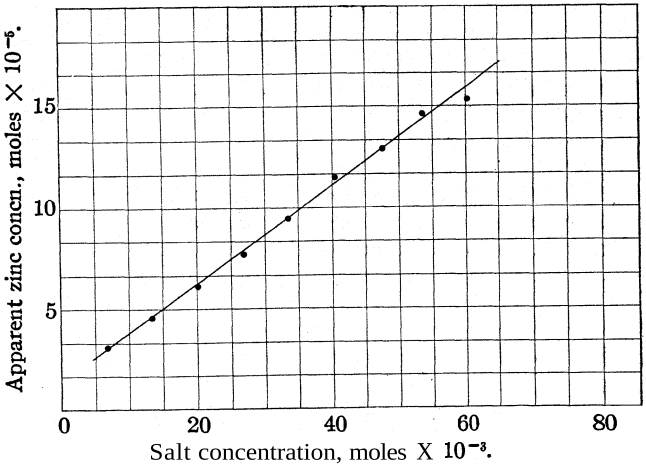

Fig. 3.

Method of Analysis.—The method of analysis based upon the foregoing experiments and which has been adapted to biological material is as follows.

Dissolve the ash of material obtained by low temperature ashing[6] in 6 *N* redistilled hydrochloric acid and hot water. For quantitities approximating the ash of 100 cc. of blood, dilute the solution to 75 cc., add 5 g. of pure sodium citrate, 2 mg. of copper as sulfate and a sufficient amount of thymol blue indicator. Add dilute potassium hydroxide solution until the solution becomes yellow and then add brom chlor phenol blue. If the solution is bluish at this point, add dilute acid until the yellow color is just restored. Saturate the cold solution with hydrogen sulfide gas, filter out the zinc and copper sulfides, washing well to free from iron salts as much as possible. Dissolve the sulfides in nitric acid and hydrochloric acid, evaporate to dryness twice with hydrochloric acid, dissolve the residue in hydrochloric acid and repeat the above procedure omitting the addition of sodium citrate. In the absence of buffer the adjustment of acidity is much

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[6] P. K. Thompson, J. *Ind. Hyg.* 7, 358 (1925).

sharper and requires more care. Dissolve the reprecipitated sulfides as before, add 5 cc. of 6 *N* hydrochloric acid to the residue and 20 cc. of water. Slowly saturate the cold solution with hydrogen sulfide and filter. The filtrate contains the zinc as chloride. Evaporate to dryness and dissolve the residue in 4 to 5 drops of 6 N hydrochloric acid and a little water. The solution of the residue at this point is occasionally refractory, and it is necessary to see that it is moistened throughout with acid and warmed slightly before the addition of water. Transfer to a 25-cc. volumetric flask. To an aliquot portion (5 or 10 cc.) of this solution add 10 cc. of 0.1341 N potassium hydroxide and exactly neutralize the excess of potassium hydroxide with 0.10 N hydrochloric acid, adding exactly 1 cc. of acid in excess. Dilute almost to 50 cc., add 1 cc. of 2% potassium ferrocyanide solution, adjust exactly to a volume of 50 cc. and thoroughly mix at once. This solution is now 0.002 N with respect to acid and 0.0268 molar with respect to potassium chloride. The nephelometric standards should be prepared in exactly the same way in order to insure equivalent salt and acid concentrations. The most suitable range for comparison is that of standards containing 0.20 to 0.25 mg./50 cc. matched against solutions of nearly the same opacity as the unknown. If Nessler tubes are used, colorless glass tubes should be selected and the bottoms and a band about the meniscus blackened. Especial attention must also be given to the quality of light in this case. The standards for Nessler tubes should vary from 0.05 to 0.50 mg. in steps of 0.05 mg.

Analysis of biological material—particularly blood—for minute amounts of zinc is much facilitated by the above method. The conditions for exact separation and estimation are easily fulfilled and interference by other metals is minimized. In order to determine its adequacy for blood analysis, a zinc-free solution representing the relative concentration of the various inorganic salts present in blood was prepared. Five cubic centimeters of this solution represented the amount of ash from 100 cc. of blood. To 5-cc. portions of this solution amounts of zinc varying in quantity from 0.50 to 1.40 mg. were added and the solutions analyzed. In three series of experiments comprising thirty-three analyses of this type, the average error was ±0.06 mg. While this does not represent an extraordinary degree of accuracy, in view of the expediency attained it seems particularly suitable for the amounts of zinc normally present in biological material.

Summary

In the analysis of biological ash for traces of zinc, the separation of the latter from certain other metals and from iron in particular is most accurately made by co-precipitation with copper as the sulfide at a C_{H} of 10^{-3}. The nephelometric estimation of zinc as the ferrocyanide gives accurate results only within definite limits of acidity and salt concentration. Suitable conditions for this have been found at a C_{H} of $10^{-2.3}$ and at a salt concentration of 0.0268 molar with respect to potassium chloride.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

COMPOUND FORMATION IN THE SYSTEM NAPHTHALENE–META-DINITROBENZENE

BY EVALD L. SKAU

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In a recent article Puschin[1] arrives at the conclusion that the supposed compound between naphthalene and m-dinitrobenzene is really only a mechanical mixture of these two substances. He has repeated the work of Kremann[2] on the binary freezing point diagram of these sompounds, which shows a range for compound formation, and he states that the true diagram is of the simple single eutectic type.[3] As a further argument against compound formation he presents data on heats of combustion obtained for the supposed compound and for an equimolecular mixture of the two substances in question.

In the course of some freezing point work done three years ago, we had occasion to construct the freezing point diagram for this binary system, making our measurements by two methods either of which would have been adequate. We found by both methods that Kremann's diagram is substantially correct and that the system has the characteristics of one showing compound formation.

Binary Freezing Point Data

Materials.—A sample of Kahlbaum m-dinitrobenzene was purified by systematic fractional crystallization from benzene making use of centrifugal filtration tubes.[4] The pure naphthalene was prepared by successive sublimation of Kahlbaum naphthalene.

Method and **Results.**—The freezing points were determined by the method and apparatus previously described[5] and a few pertinent points were determined by the visual method described by Johnston and Jones,[6] which involves observing the temperature at which the last crystal disappears when the specimen is heated extremely slowly. The data are given in Table I, the temperatures being accurate probably to within 0.25" in all cases.

Discussion of Freezing Point Diagram

Our data are reproduced in Fig. 1, the heavy dots representing the values determined by the freezing point method mentioned, the circles

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[1] Puschin, *Z. physik. Chem.*, 124, 16 (1926).

[2] Kremann, *Monatsh.*, 25, 1283 (1904).

[3] The freezing point determinations were evidently made by B. E. Kitran and were published separately by him in another paper, *Farmaceutski Vjesnik*, 14,777 (1924).

[4] Skau, J. *Phys. Chem.*, 33, 951 (1929).

[5] Skau and Saxton, THIS JOURNAL, 50,2693 (1928).

[6] Johnston and Jones, J. *Phys. Chem.*, 32,593 (1928).

TABLE I

FREEZING POINTS OF BINARY MIXTURES OF NAPHTHALENE AND *m*-DINITROBENZENE

Mole % of naphthalene	F. p., °C.	Equilib. temp. (visual method), °C.	Eutectic flat, °C.
0.00	90.1		
14.35	80.5		
29.83	68.6		
36.42		62.5	
40.43	58.6		50.8
44.45		54.4	
46.23	50.8		
57.54	50.5		49.7"
56.95	50.4		
55.36	50.7	51.1	
53.68	50.8		
51.27	51.1		
62.53	52.8		49.7[a] 49.7
62.65		53.3	
68.42		58.6	
81.41	68.7		
100.00	80.0		

[a] By heating curves.

those obtained by the visual method. These two types of measurement, which involve approaching equilibrium from opposite directions, show very good agreement. This proves that the diagram represents real equilibrium conditions and that our method of determining freezing points is valid, even in the neighborhood of the equimolecular mixture where Puschin claims that accurate determinations are impossible owing to a tendency on the part of the liquid to undercool.

The only type of curve which can be drawn through our points is one indicating compound formation with two eutectics, one at 49.7" for about 59.5 mole per cent. of naphthalene and the other at 50.8° for about 46.3 mole per cent. The compound melts at 51.2". The eutectic temperatures were determined for three mixtures. The higher one, 50.8°, was determined from the second break in the cooling curve. The lower one, 49.7°, was determined from the "flat" on the heating curves for the two mixtures in question and for one of these latter mixtures it was also checked by cooling curves. In the case of the cooling curves, after the first break the mixture cooled to about a degree below the eutectic and the temperature then rose to the eutectic "flat," the temperature of the surroundings still remaining below that of the melt. It is not conceivable, therefore, that the temperature reading so obtained could be higher than the true equilibrium value. On the other hand, it is well known that the equilibrium temperature obtained from heating curves is apt to be too high rather than too low.[7] Thus our data show that there must be two eutec-

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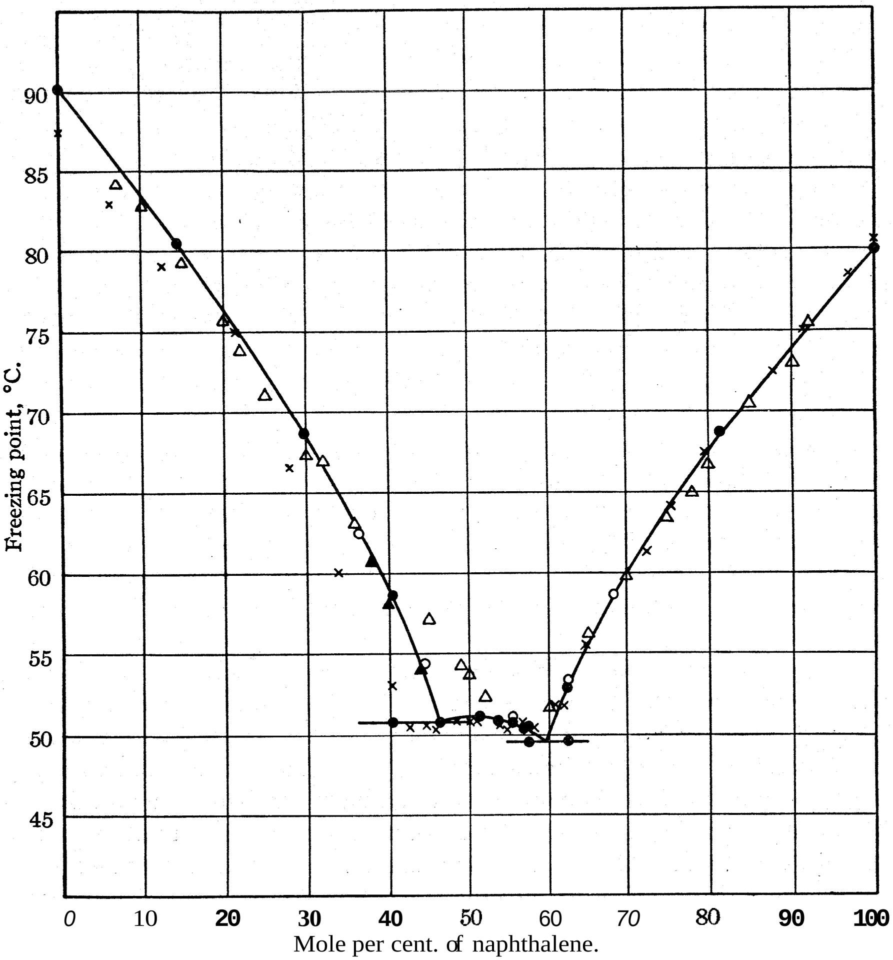
[7] White, Am. J. Sci., 28,453,477 (1909).

tics, one certainly not lower than 50.8°, the other certainly not higher than 49.7". As a matter of fact, these values are probably correct to within a few tenths of a degree, as is shown by the fact that the value obtained for the 49.7° point by the heating curve method was checked by the cooling curve method to within 0.1°.



●, Cooling curve method; ○, **visual** method; △, **Puschin**; ×, Kremann; A, **Kitran.**

Fig. 1.—Binary freezing point diagram of the system naphthalene–m-dinitrobenzene.

Puschin's results and those of Kremann have been included in Fig. 1, the former by triangles and the latter by crosses. Our results seem to agree in general with those of Kremann except that his values for the *m*-**dinitrobenzene** side of the **diagram are** from 2 to 6° low. His **two**

eutectics are 50.5 and 50.3" and his melting point for the compound is 50.8° Puschin's results seem to agree reasonably well with ours down to within a few per cent. of the compound region and then show marked deviations, his values being considerably higher than ours. Be has evidently accepted all of Kitran's[3] values except three in this region which he has rejected. These, which have been represented in Fig. 1 by black triangles, show good agreement with our curve.

The diagram which Puschin draws for the binary system does not seem to be justified by his freezing point determinations. In order to make the two branches meet at a single eutectic (at 56% naphthalene and 51.0") he has distorted the curves considerably and even then the curve, as he has drawn it, does not pass through his experimental points. An examination of his Table I shows that his values for the eutectic temperatures for the various compositions are really not at variance with our diagram showing two eutectics. For percentages of naphthalene less than 50% his eutectic temperature is 51.0"; and for the 56% composition (which he calls the eutectic point) and greater percentages his highest eutectic "flat" comes at 50.0°. These are approximately the values which would be predicted from our Fig. 1.

Unfortunately we have no data for a composition of exactly 56%. The curves for 55.36 and for 56.75%, however, have none of the characteristics of a mixture within 1% of the eutectic composition. On the other hand, our 46.23% mixture gave a typical eutectic cooling curve and the 51.27% mixture gave a curve such as one would expect from a 1:1 compound containing a per cent. or two of one of the constituents in excess.

Puschin presents two reasons for his belief that his simple eutectic diagram represents the facts better than Kremann's diagram. His first is based upon the fact that when the length of the eutectic halt obtained in his freezing point determinations is plotted against the composition, there is a maximum at a composition of 56 mole per cent. of naphthalene. We do not consider the results of this indirect method, a method which at best can be regarded as only approximate, as sufficient evidence to overthrow the actual experimental freezing point results. His second reason is based upon the relative heats of combustion of the supposed compound and of an equimolecular mechanical mixture, but it seems to us that his experimental results do not justify his conclusion. Puschin points to the work of N. N. Nagornow,[8] who determined the molecular weight of the compound in benzene, found practically complete dissociation, and then determined the heat of solution of the supposed compound and of the equimolecular mechanical mixture, finding a difference of 2% (actually 165 g. cal. per mole). The difference obtained by Puschin for

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[8] Nagornow, *J. Russ. Phys.-Chem. Soc.*, **51**, 301 (1919).

the heats of combustion of two such samples is 0.18% (actually 12 g. cal. per gram), which he states is within his experimental accuracy. Due to an oversight, Puschin evidently came to the conclusion that these two results are conflicting. Actually, of course, the absolute difference rather than the percentage difference must be considered, so that his results prove merely that the heat of reaction to form the compound is less than **(12** × 296) or about **3550** g. cal. per mole, which is not at variance with Nagornow's findings.

It should also be pointed out that the possibility of compound formation would not be definitely eliminated on theoretical grounds by *a* zero heat of reaction, for it would still be possible to have a negative free energy change.

Further Evidence of Compound Formation.—Several other investigators who have studied this system have come to the conclusion that it exhibits compound formation. Hepp, who originally discovered the supposed compound, claims that he isolated it in a distinct crystalline form[9] from an equimolecular solution of the two compounds in benzene. Buehler and Heap[10] report its isolation by recrystallization from absolute alcohol.

Olivari[11] confirmed Kremann's freezing point diagram, as we have on the basis of actual freezing point determinations. He found two eutectics, one at **49.5"** for a composition of **59** mole per cent. of naphthalene and the other at 50.3° for **42.5** per cent. He gives the freezing point of the compound as **50.5".** Furthermore, he reports that he was able to verify the existence of two eutectics by plotting the length of the eutectic halt against the composition. Viscosity data for the system also points to compound formation. Kurnakow[12] determined the binary viscosity–composition diagram for the system and found that, though the liquid gave normal results at 90°, there was distinct evidence of a compound present in the liquid state at 52°.[13]

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[9] Hepp, **Ann., 215, 379 (1882):** "dicke prismatische Nadeln, welche eine Länge von 5 cm. und mehr erreichen. Sie sind glashell, hart und sehr bruchig, werden aber an der Luft sehr bald trübe, in Folge von Abdunstung von Naphthalin, und schmelzen bei 52 bis 53°. Die durch die Analyse ermittelte procentische Zusammensetzung passt fur die Formel $C_6H_4(NO_2)_2$-$C_{10}H_8$."

[10] Buehler and Heap, THIS JOURNAL, 48,3168 **(1926).**

[11] Olivari, *Rend. soc. chim. ital.,* **[2] 3, 90 (1911).** Olivari represents his freezing point data graphically only, giving no numerical results except for the two eutectic points and for the equimolecular mixture. The graphical representation of his data is plotted on such a small scale that it is impossible to read off the values with any accuracy. They have therefore been omitted from Fig. **1.** His curve would, however, if reproduced fall between ours and that of Kremann.

[12] Kurnakow, *Z. anorg. allgem. Chem.,* **135,** 81 **(1924).**

[13] The density data for the system published in the same paper did not indicate compound formation, but this cannot be regarded as positive evidence, judging from the data of other systems mentioned where compound formation is unquestioned.

Summary

The freezing point–composition diagram of the system naphthalene–*m*-dinitrobenzene has been redetermined, the freezing points being measured by two methods which involve approaching the equilibrium from opposite sides. The resulting diagram is of the compound formation type and thus corroborates substantially the diagrams of Kremann[2] and of Olivari,[11] and disagrees with that of Puschin.[1] Exception is taken to the arguments of Puschin against compound formation in this system, and viscosity data are cited as further evidence showing that the system is not of the simple eutectic type as Puschin claims.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

CONCENTRATION OF HYDROGEN PEROXIDE SOLUTIONS

BY CHARLES D. HURD AND M. P. PUTERBAUGH

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Numerous methods have been described for the concentration of hydrogen peroxide solutions to 60–90% strength, but apparently it is impossible to exceed 90–91% by evaporation or distillation methods. An efficient plan for such a process is that of Maass and Hatcher,[1] but in spite of its efficiency this method is made rather cumbersome by requiring an all-glass apparatus with ground-glass joints and also a sulfuric acid pump. Such special equipment detracts materially from the general usefulness of this process.

The method described in the present paper also is capable of concentrating hydrogen peroxide solutions rapidly to 90% strength, and the apparatus required is merely the simple equipment for distillation and for vacuum distillation. The essence of the method is to add an immiscible volatile liquid such as a hydrocarbon and to distil the mixture. This modified steam-distillation leaves a residue of concentrated hydrogen peroxide after the water and hydrocarbon have distilled away. The method is simple and by controlling the conditions one may obtain nearly any degree of concentration up to 90-91%. It is necessary only to mix about one volume of peroxide solution with two volumes of hydrocarbon. By ordinary distillation with xylene a 3% solution may be concentrated to about 30% strength, and by using *p*-cymene and distilling in a vacuum, a 30% solution may be concentrated to about 90%. A similar method was found to be very satisfactory for the concentration of hydrazine hydrate[2] solutions.

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[1] Maass and Hatcher, THIS JOURNAL, 42, 2552 (1920).

[2] Hurd and Bennett, *ibid.*, 51, 265 (1929).

Some of the results may be briefly summarized. With xylene as the hydrocarbon it was possible to effect a concentration of 3% to either 17% or to 25–30% by ordinary distillation. For the former, distillation was interrupted when the volume of the aqueous residue was about one-tenth its original volume. For the latter, the distillation was interrupted at one-twentieth the volume, and the yield of 30% peroxide by this method was about 60%. It was found that 20-30% of the original peroxide was decomposed into oxygen gas, a decomposition which was caused by the high temperature (about 100°) of the distillation. Starting with 30% hydrogen peroxide, further concentration to a peroxide of 45–60% strength was attainable by another distillation but higher than 60% by this method was not realized. Vacuum distillation at 20-30 mm. with xylene effected a concentration of 30% hydrogen peroxide solution to only 44% (yield, 86%), so xylene was discontinued in favor of a higher-boiling hydrocarbon for the vacuum distillation studies.

p-Cymene and tetralin were both found to be satisfactory, but the residual concentrated hydrogen peroxide from tetralin always assumed a deep yellow color. The peroxide from cymene was colorless, and cymene was the most satisfactory of the three hydrocarbons tried. Indeed, it was found possible to start with 30% hydrogen peroxide and concentrate this to 89% strength in one operation in 60% yields merely by distilling it, admixed with cymene, in the vacuum of a water pump. The distillation temperature of the mixture when cymene was used at 25–32 mm. was 52–55'. Losses under these conditions were very small, since the total peroxide in the aqueous distillate and in the undistilled portion was 91–96% of the original quantity. The material of 88–91% purity which was produced crystallized readily in an ice–salt mixture and was thus capable of further concentration to pure hydrogen peroxide by the method of Maass and Hatcher, who found that several such recrystallizations were necessary before 100% purity was attained.

Since commercial solutions of hydrogen peroxide contain non-volatile preservatives, it is obvious that such substances, if originally present, will remain either in the residual concentrated peroxide solution or in the supernatant residual hydrocarbon layer. Most of our work was performed either with the 30% hydrogen peroxide of commerce or with the aqueous, peroxide-containing distillates from our own experiments. Such distillates necessarily contained no non-volatile preservatives, but the experiments with them seemed identical with the others. It is evident that a distilled peroxide solution should be used as a starting material whenever the presence of foreign material in the concentrated peroxide is objectionable.

Experimental Part

Materials Used.—Both the **3%** (Mallinckrodt) and the 30% (**Merck's Superoxol**) commercial solutions of hydrogen peroxide were used in this work. The former **was**

stated to contain acetanilide (0.04%), whereas traces of acidic preservatives[3] (oxalic, no more than 0.035%; sulfuric, 0.015%; and lesser amounts of hydrochloric, hydrofluoric and phosphoric acids) were stated to be in the latter. In addition to these commercial sources of hydrogen peroxide solutions, several of the "aqueous distillates" which are mentioned below were also concentrated by the present method.

Distillation of Hydrogen Peroxide with Xylene at Atmospheric Pressure.—One volume of the peroxide solution was admixed with about two volumes of xylene in a **pyrex** distilling flask. The flask was attached in the usual way (cork stoppers) to a condenser and receiver. The flask was heated by an oil-bath and the distillation was continued until 80–90% of the xylene had distilled over. The temperature of the vapor was noted. The two layers of both the residue and the distillate were separated, measured and the aqueous portions analyzed by titration with standard permanganate. The data are summarized in Table I.

Concentration of Hydrogen Peroxide Solutions by Vacuum Distillation **with *p*-Cymene.—The** apparatus employed in this case was the customary one for organic vacuum distillations. Thus a Claisen flask was attached to a condenser, which in turn

TABLE I

DATA ON DISTILLATION EXPERIMENTS OF MIXTURES OF HYDROGEN PEROXIDE, WATER AND HYDROCARBONS

Original H_2O_2 soln.					Hydrocarbon		Aqueous distillate		Residual H_2O_2			Recov. H_2O_2 (distillate + residue),	
Concn., % by wt.	Vol., cc.	Distn. temp., °C.	Press., mm.	Duration of distn., hrs.	Distillate, cc.	Residue, cc.	Vol., cc.	Concn., % by wt.	Vol., cc.	Concn., % by wt.	Yield, %	g.	%
					Xylene								
3	900	93	750	6	1870	,127	835	0.3	59	25.1	60	18.5	68[a]
3	900	93	750	6	1785	200	785	0.3	110	17.1	73	22.3	82
17.5	127	94	750	1	187	11	81	3.5	43	30.5	62	17.5	74
30	100	98	750	1	168	30	58	5.8	41	46.3	67	25.8	77
30	100	37	30	0.6	193	45	41	5.1	56	43.6	85	30.7	92
30	100	98	750	1	175	25	62	4.7	37	45.4	59	22.7	68
30	90	97	750	1.5	161	37	58	4.5	31	59.9	76	25.7	85
46	70	98	750	0.6	111	37	34	9.1	33	48.7	51	22.3	60
30	100	99	750	1.2	164	30	58	4.4	42	54.6	84	30.6	91
					Cymene								
49	30	46	23	1	30	30	17	17.9	12	80.0	74	16.1	92
60	30	52	29	0.6	22	37	12	27.0	17	78.9	80	21.4	96
55	41	55	28	1	55	25	24	39.0	13	90.3	60	27.0	98
79	16	56	29	0.25	28	9	8	62.6	8	88.5	58	16.1	96
80	8	52	25	0.25	6	14	3	47.6	5	90.6	75	8.1	95
85.8	15	55	29	0.1	12	18	3	67.0	11	88.3	76	15.9	91
30	80	57	32	1	91	66	67	13.4	13	88.8	60	25.5	95
30	100	44	10	1.3	150	45	83	18.1	14	82.5	47	31.5	94'
					Tetralii								
60	61	52	27	0.5	15	83	30	29.0	30	84.3	76	44.1	97
87	13	38	7	0.2	4	24	3	70.7	9	90.2	73	14.1	91

[a] In this run 2900 cc. (26°, 750 mm.) of oxygen was collected. This is equivalent to 29% of the original hydrogen peroxide.

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[3] After reading the manuscript, the Referee commented that "the 30% peroxide now placed on the market contains salicylic acid."

was attached to a receiver, manometer and water pump. Rubber stoppers were satisfactorily used throughout, since they were not appreciably attacked by the hydrocarbon at the temperature employed. A water-bath, kept at 70–75°, was used to heat the Claisen flask. Since our experiments were designed to show the fate of all substances used, the receiver was kept in an ice-bath to minimize losses from the distillate. Were concentration of the peroxide the only goal, this ice-bath could be omitted. Usually, two volumes of cymene were placed in the Claisen flask with one volume of either 30 or 60% hydrogen peroxide solution. The distillation was stopped to analyze the various fractions before all of the cymene had distilled. These data also are collected in Table I.

Similar vacuum distillation experiments were also conducted with xylene and with tetralin. Some experiments with cymene and with tetralin were carried out with an oil pump, but no advantage was gained thereby. The concentrated hydrogen peroxide obtained when tetralin was used was always yellow in color. The cause of the coloration was not investigated.

Summary

If hydrogen peroxide solutions are vacuum distilled with *p*-cymene, a peroxide of 88–91% strength may be obtained readily. The yield of this concentrated material which remains undistilled is 60–76% and most of the remaining peroxide is to be found in the distillate. Actual losses, therefore, are negligible since a 91–98% recovery was always realized when the distillation temperature was kept below 57°. The simplicity of the apparatus and the rapidity of the concentration are also very desirable features.

Tetralin behaves like cymene in this respect, but it imparts a yellow color to the concentrated peroxide. Xylene also was studied but its high vapor pressure, as compared to cymene, makes it undesirable for use at 25–30 mm. pressure. With distillation at atmospheric pressure the losses due to decomposition of the peroxide into oxygen become quite appreciable.

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[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OF PRINCETON UNIVERSITY]

THE SENSITIVITY AND APPLICABILITY OF THE PICRIC ACID TEST FOR POTASSIUM

BY EARLE R. CALEY

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The fact that an alcoholic solution of picric acid can be used as a reagent for potassium has been frequently noted in the literature of analytical chemistry. There exist, however, no quantitative data regarding either the sensitivity of this reagent toward the potassium ion or the allowable concentrations of other ions that can be present without causing interference. The present experiments were undertaken in order to determine these points and to find the optimum conditions for this reaction.

Experimental Part

Preparation of the **Reagent.**—The reagent used in these experiments, and the one found most suitable, was prepared by drying the moist picric acid of reagent grade in an air oven at 70–80°, recrystallizing the dried product from benzene and, after allowing the drained crystals to stand exposed to the air until the adherent benzene had evaporated, dissolving the final product in 95% ethyl alcohol to form a solution saturated at room temperature. Recrystallization from benzene was found necessary with the particular grades available since alcoholic solutions made from the picric acid not so treated developed a slight turbidity, on being added to distilled water, due to the presence of impurities. Experiments were also made with reagents consisting of solutions of picric acid in absolute alcohol, dilute alcohol and various organic solvents, but these attempts led to no useful results.

Characteristics of the Reaction.—When a saturated alcoholic solution of picric acid is added to an aqueous solution of an alcohol-soluble potassium salt, preferably the chloride, a well-defined crystalline precipitate of anhydrous potassium picrate results. With concentrated solutions precipitation is almost instantaneous, while with dilute potassium solutions the crystals separate only after some minutes. The chief factors influencing the reaction, from an analytical view-point, were found to be the concentration of the potassium solution, the ratio of the volume of reagent to the volume of the test solution, the influence of the time of reaction and the effect of the presence of other substances.

The Effect of Volume of Reagent.—The ratio between the volume of the saturated alcoholic solution of picric acid and the volume of the test solution is of marked influence on the sensitivity of this reaction. In the experiments on this point varying volumes of reagent were added to fixed volumes of solutions containing varying concentrations of potassium chloride. Table I shows the results obtained when using 1.0 cc. of potassium chloride solution.

TABLE I

THE EFFECT OF VOLUME OF REAGENT (REACTION TIME, 30 MINUTES)

Potassium present, g.	Reagent volume 2.5 cc.	5 cc.	7.5 cc.	10 cc.	15 cc.
0.0006	No ppt.	No ppt.	No ppt.	No ppt.	No ppt.
.0007	No ppt.	No ppt.	Doubtful	No ppt.	No ppt.
.0008	No ppt.	No ppt.	Slight ppt.	Doubtful	No ppt.
.0009	No ppt.	Doubtful	Fair ppt.	Slight ppt.	No ppt.
.0010	Doubtful	Slight ppt.	Good ppt.	Fair ppt.	No ppt.

Similar results were obtained when using volumes of potassium chloride solution greater or less than 1.0 cc. In all cases the optimum results were obtained when the volume of reagent was from seven to eight times that of the test solution.

Effect of Time of **Reaction.**—Since the reaction between potassium ions and picric acid in alcoholic solution is not instantaneous with small concentrations of potassium, experiments were performed to determine the effect of reaction time on the possibility of detecting small amounts of potassium. In these experiments 7.5 cc. of reagent was added to 1.0 cc. of potassium chloride solution and the effect observed after different elapsed times. The results appear in Table II.

TABLE II

THE EFFECT OF REACTION TIME IN THE PICRIC ACID TEST FOR POTASSIUM

Potassium present, g.	Reaction time 1 min.	5 min.	30 min.	24 hrs.
0.0006	No ppt.	No ppt.	No ppt.	No ppt.
.0007	No ppt.	Doubtful	Doubtful	Very slight ppt.
.0008	No ppt.	Very slight ppt.	Slight ppt.	Slight ppt
.0009	No ppt.	Slight ppt.	Fair ppt.	Fair ppt.
.0010	No ppt.	Slight ppt.	Good ppt.	Good ppt.

It will be seen that, aside from the action during the first few minutes, a prolonged duration of the test affects but little the possibility of detecting potassium in concentrations that give no reaction in shorter periods.

Sensitivity of the Reaction.—From the various experiments it was concluded that, when the volume of reagent is from seven to eight times that of the test solution and a thirty-minute period is allowed before observing the results of the test, one part of potassium can be detected with certainty in twelve hundred and fifty parts of solution, *i. e.*, the sensitivity of the reaction is 1:1250. This sensitivity can be further increased to 1:1650 by saturating the reagent with potassium picrate, but this procedure is not to be recommended.

Interfering Substances.—Owing to the nature of the reagent it is at once apparent that salts insoluble in strongly alcoholic solution cannot be present. In practice this restricts the application of the test to chloride solutions. The solutions tested should preferably be neutral. Strongly acid solutions reduce the sensitivity of the test. The following table shows the results of some of the experiments that were made to determine the specific action of the positive ions usually associated with potassium. In these experiments 1.0 cc. of solution containing varying concentrations of the metallic chlorides was treated with 7.5 cc. of reagent.

TABLE III

REACTIONS OF SODIUM, LITHIUM AND MAGNESIUM WITH PICRIC ACID REAGENT

Element	Concn., g./cc.	Reaction time, 5 min.	Reaction time, 30 min.
Na	0.0040	No ppt.	No ppt.
Na	.0050	Doubtful	Very slight ppt.
Na	.OM5	Slight ppt.	Good ppt.
Na	.0100	Good ppt.	Good ppt.
Li	.1000	No ppt.	No ppt.
Mg	.1000	No ppt.	No ppt.

Ammonium, rubidium and cesium behave like potassium but, since the former is readily removed and the two latter are practically never met with in weighable quantities, the interference from these elements is of no importance. The interference from sodium is more serious and prevents the use of the reagent for detecting potassium in the presence of sodium unless dealing with small residues of alkali chlorides. It should be mentioned, however, that the crystalline precipitates formed by potassium and sodium are quite different in appearance. The former yields short prisms and needles which, particularly when the amount of potassium is small, present an iridescent appearance in strong light while the latter forms long hair-like crystals which never present an iridescent appearance.

Conclusions

The interference of sodium in the above reaction restricts its use to a greater extent than has been generally supposed. Regardless of this limitation, however, it may be employed as a confirmatory test for potassium after the approximate separation of the two elements or for the examination of small residues of alkali chlorides. For these purposes it has certain advantages over the usual reagents for potassium. It is more sensitive than perchloric acid, chloroplatinic acid or tartaric acid and, while not as sensitive as sodium cobaltinitrite, it has the advantage of possessing much greater stability since solutions of picric acid in alcohol appear to keep indefinitely.

PRINCETON, NEW JERSEY

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

THE KINETICS, STATICS AND ENERGETICS OF THE THERMAL REACTION $CH_2I-CH_2I = CH_2{=}CH_2 + I_2$ IN CARBON TETRACHLORIDE SOLUTIONS

BY MILTON J. POLISSAR

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Introduction

The object of this research was to determine the kinetics of the decomposition of ethylene iodide in carbon tetrachloride solutions. Since the number of reactions that proceed in a direct and simple manner is limited, it was of great interest to find that this one follows a fairly simple law through a large range of concentrations and temperatures.

The results are of further interest since it was possible, by assuming a simple mechanism of reaction, to give a complete interpretation not only of the so-called "energy of activation" but of the actual magnitude of the rate as well. The plausibility of the interpretation is enhanced by the fact that it can be applied successfully to two similar reactions previously studied by other investigators. One of the reactions referred to is the decomposition of ethylene iodide in alcoholic solutions, in the presence of iodide ions. The other is the decomposition of phosgene in the gaseous phase.

Experimental Methods

Materials Used.—Commercial carbon tetrachloride was purified in the following way. Chlorine was bubbled through a large volume of the liquid until the concentration of the former reached about 0.1 N. Enough iodine was added to make its concentration about 0.015 N. The resulting mixture was allowed to stand for forty-eight hours and then it was refluxed near its boiling point for three hours. The halogens were extracted with 0.5 N sodium hydroxide and the organic phase was washed with 0.5 N hydrochloric acid and finally with water.

The carbon tetrachloride was dried by refluxing for sixteen hours over granulated calcium chloride, followed by five hours of refluxing over phosphorus pentoxide, both carried out near the boiling point. Finally, it was distilled over a fresh portion of phosphorus pentoxide into a carefully dried all-glass wash bottle.

Kahlbaum ethylene iodide was used. Although the solid contained some iodine because of partial decomposition, no attempt was made to purify it. Whenever an iodine-free solution was wanted the iodine was removed by shaking the solution with mercury.

In some of the experiments the initial iodine content was increased by adding a solution of iodine in carbon tetrachloride. The latter was prepared by dissolving "P. W. R." iodine crystals in the purified carbon tetrachloride.

Preparation of the Solutions.—The stock solutions were prepared by dissolving a weighed amount of the partially decomposed iodide in a weighed amount of carbon tetrachloride. The solution was titrated for free iodine. The ethylene iodide content was then readily calculated. More dilute solutions were obtained by the addition of carbon tetrachloride to the stock solutions.

Rate Measurements.—The rate of decomposition of the iodide is very small at ordinary temperatures. For this reason most of the measurements were carried out in the range 120 to 150°. In an ordinary experiment several (5 to 12) 8-cc. samples were sealed in glass bombs prepared from 18-mm. pyrex test-tubes. For rate measurements at the highest temperatures, at which the total duration of the experiment was short, the bombs were mapped in tin foil. For measurements at lower temperatures ordinary toweling was used.

Suspended from copper wires, the samples were immersed in the thermostat and withdrawn at convenient intervals. Each bomb was opened and emptied into a weight buret. A weighed amount was introduced into a slightly acidified solution of potassium iodide and titrated with 0.05 or 0.005 N sodium thiosulfate solution, depending upon the iodine concentration. In the later experiments a known amount of the solution was withdrawn by means of a calibrated pipet.

Equilibrium Measurements.—The same general procedure was used as in the rate measurements, with the only difference that the bombs were kept in the thermostat for longer periods, depending on the concentration of the solution and on the temperature. In the experiments at 122 and 132° the reversibility of the reaction was tested. The samples were divided into two groups. One group of samples was first kept at a temperature 10° higher than the temperature under investigation for a time long enough to establish equilibrium. After that the thermostat was cooled and the second group of bombs added.

Temperature Control.—The temperature of the thermostat was kept constant to 0.1°. The temperature regulator, designed by the author to allow a rapid change of the temperature setting was described elsewhere.[1]

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[1] Polissar, THIS JOURNAL, 52, 636 (1930).

The Kinetics of the Decomposition

Preliminary experiments have shown that the decomposition is autocatalytic and that iodine is the accelerating agent. From an analysis of eight experiments performed at the same temperature, it appeared that the rate is proportional to the first power of the ethylene iodide and to the square root of the iodine concentrations. This kinetic relationship was next tested experimentally through a large range of temperatures and of concentrations and was found to hold true to within a very few per cent.

Let S be the total iodine content of the solution, free and in combination, and let x be the free iodine content. The kinetic equations and the rectified integrated equations can be represented as follows

$$d(I_2)/dt = dx/dt = k_1(EI_2)(I_2)^{1/2} = k_1(S - x)x^{1/2} \qquad (1)$$

$$y - y_0 = k_1(t - t_0), \text{ where } y = \frac{1}{\sqrt{S}} \ln \frac{1 + \sqrt{\frac{x}{S}}}{1 - \sqrt{\frac{x}{S}}} \qquad (2)$$

It will be seen from Equation 2 that the assumed kinetic law can be tested by plotting the experimental results on a y–t diagram. If the law is correct, then points corresponding to a single experiment must fall on a straight line; the slopes of all the lines corresponding to measurements at a single temperature must be the same, and equal to k_1.

In Figs. 1 and 2 are given the results of measurements made at six different temperatures, ranging from 40 to 152'. The iodine concentrations worked with ranged from 1.5×10^{-5} to 0.1 equivalent per kilogram; the ethylene iodide concentrations ranged from 0.011 to 0.19 equivalent per kilogram.

For the sake of compactness the results of measurements made at three different temperatures were plotted on the same diagram. The heavy vertical lines separate the three regions. In Fig. 1 the experiments at each temperature were divided into two groups. Those of short duration were shown in the lower part of the plot; those of long duration, in the upper part. Since both the vertical and the horizontal scales have been doubled, the slope remained unchanged. In Fig. 2, which contains the summary of experiments with widely different rate constants, it was necessary to use different scales for the ordinates in the three regions. Furthermore, with the large scales used in the 75 and 40° regions, it was necessary to shift some of the lines in the vertical direction in order to bring them into the figure.

At the top of each temperature region is given the composition diagram for all the solutions used at the temperature in question. The 45° lines drawn on an ethylene iodide–iodine field show not only the initial composition of each solution but the concentrations of the two substances during the whole course of the experiment as well.

In some of the experiments the possible experimental error in y due to titration alone was of the same order of magnitude as the change in y due to the reaction. In such cases the size of the circle was made to indicate the experimental error.

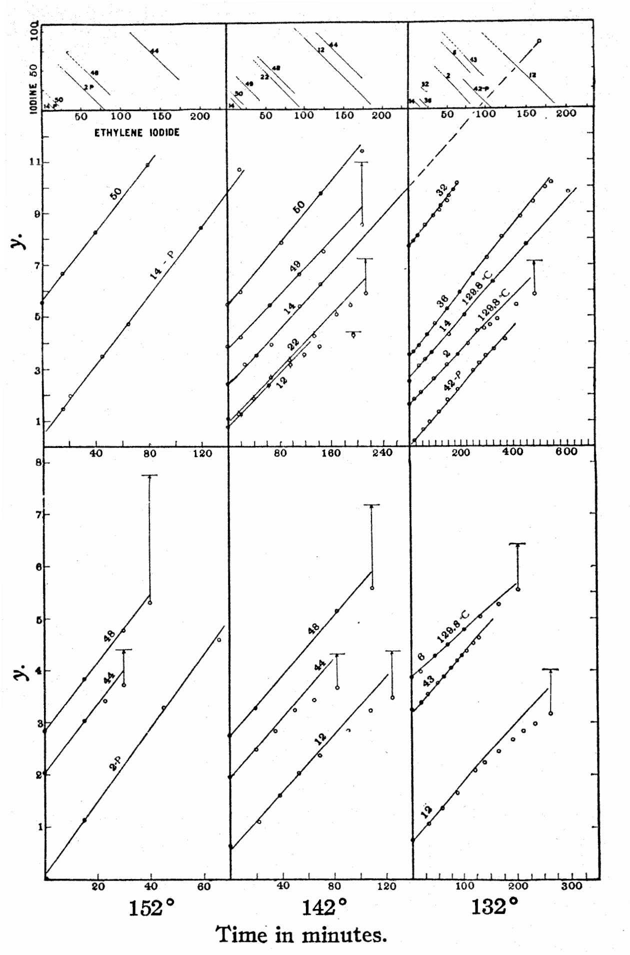


Fig. 1.

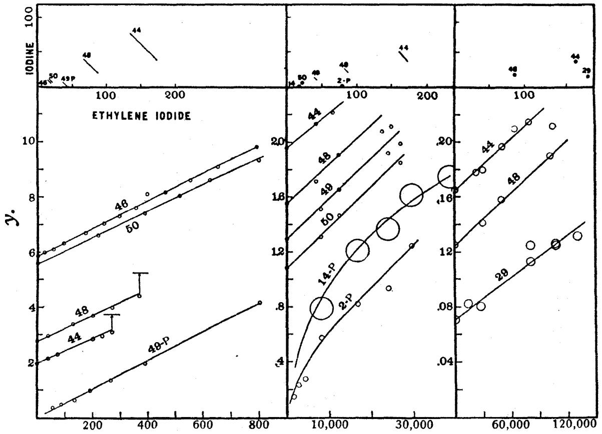
It will be seen that of the thirty-five experiments shown in the two figures all but two satisfy a linear relationship. While in some of the experiments a certain amount of curvature can be observed, the vertical arrows showing the distance of the last point from the equilibrium value of y emphasize the fact that the deflection is due to the reverse reaction. The curvature appearing in the case of R–75°–14-P and —2-P will be taken up later in connection with the discussion on the superimposed slow reaction,

Table I gives a summary of the results of all the rate measurements. The concentrations are in equivalents ($EI_2/2$, $I_2/2$) per kilogram of solution. The values of k_1 given in this table were used in Fig. 3 to test the applicability of the Arrhenius equation for a second-order rate constant. It is seen that, with the exception of the 40° value, a satisfactory linear relationship is obtained. Thus the magnitude of k_1 is given by the following two forms of the Arrhenius equation

$$\mathrm{Log}_{10}\, k_1 = 12.642 + {}^1/_2 \log_{10} T - \frac{6425.2}{T} \qquad (3)$$

$$k_1 = 4.4 \times 10^{12} \sqrt{T}\, e^{-29{,}500/RT} \qquad (4)$$

where the unit of concentration is one equivalent per kg. of solution and the unit of time is one minute.



122° 75° 40

Time in minutes.

Fig. 2.

The significance of the quantity 29,500, usually called "the heat of activation," will be taken up in the theoretical part of the paper. In the discussion on the superimposed slow reaction a possible explanation is offered for the high value of the "constant" at 40°.[2]

The Decomposition in the Absence of Iodine.—In the preceding section it was shown that the main reaction is catalyzed by free iodine present in solution. The present section deals with a number of experiments

At the time this paper was completed for publication, our attention was called to a very recent research by R. B. Mooney and E. B. Ludlam, *Proc. Roy. Soc. Edinburgh*, **49**, 160 (1929), on the thermal equilibrium between ethylene, iodine and ethylene iodide. While these investigators studied chiefly the reaction in the gaseous phase, they have also carried out a few measurements on the rate of decomposition of the iodide in carbon tetrachloride at 100°. They have found that, with the same initial ethylene iodide concentration, the initial rate was approximately proportional to the square root of the iodine content.

TABLE I

VALUES OF k_1 AT TEMPERATURES 40 TO 152

t, °C.	Soln.	$(EI_2)_0 \times 10^3$	$(I_2) \times 10^3$ Initial	$(I_2) \times 10^3$ Final	$k_1 \times 10^4$	Av.
152	44	174	10.2	101.5	760	710
	48	87.7	199	52.1	650	
	50	22.1	4.85	136	780	
	2-P	80.6	0.01	49.8	700	
	14-P	17.4	0.01	6.46	660	
142	44	174	37.5	100	263	278
	48	87.8	18.9	62.7	285	
	49	43.8	9.45	33.5	267	
	50	22.1	4.75	17.0	297	
141.1	12	186	5.0	106	268	270
	14	18.7	0.47	14.7	272 272	
140.6	22	93.5	2.53	50.4	256	240
	12	186.0	5.0	84.9	224	
132	32	23.9	18.5	25.8	127	119
	36	24.3	2.07	12.1	125	
	42-P	107	0.01	37.4	118	
	43	98.5	40.3	71.4	105	
129.8	6	81.3	44.5	71.6	95	105
	a	81.7	4.92	42.1	105	
	14	18.7	0.58	6.76	117	
	12	186	5.0	68.8	105	
122	46	19.6	4.22	9.7	49.2	47.2
	44	174	37.5	76.9	46.0	
	48	87.8	189	40.1	46.8	
	50	22.1	4.75	11.0	49.2	
	49-P	43.8	0.01	7.2	50.0	
75	44	174	37.5	52.7	0.26	0.28
	48	87.8	18.9	25.9	.28	
	49	43.8	9.45	12.6	.28	
	50	22.1	4.75	5.9	.29	
40	44	174	37.5	39.1	0.0053	0.0059
	48	87.8	18.85	19.7	.0062	
	29	191.5	16.0	17.7	.0063	

which seem to indicate that ethylene iodide decomposes, at a very slow rate, even in the absence of iodine.

To detect the presence of the uncatalyzed reaction, rate measurements were carried out with "P" solutions. The latter were prepared by vigorously shaking the ordinary solutions for a few seconds with a small amount of mercury, decanting the carbon tetrachloride phase and forcing it through a cotton plug. The resulting solutions were clear and colorless, showing that the mercury had removed practically all of the iodine

Fixing our attention on experiments 2-P and 14-P (at 75°, Fig. 2), we find an abnormally high initial slope which gradually decreases to the value yielded by ordinary solutions.[3] The physical interpretation of these results is not far to seek, if we assume the existence of a slow uncatalyzed reaction. The rate of this reaction is independent of the free iodine content of the solutions; during the early stages of the experiment, when the total iodine output is small, the effect of the superimposed reaction is appreciable. Toward the end of the experiment, when the iodine concentration is large, the catalyzed reaction completely obscures the presence of the uncatalyzed one.

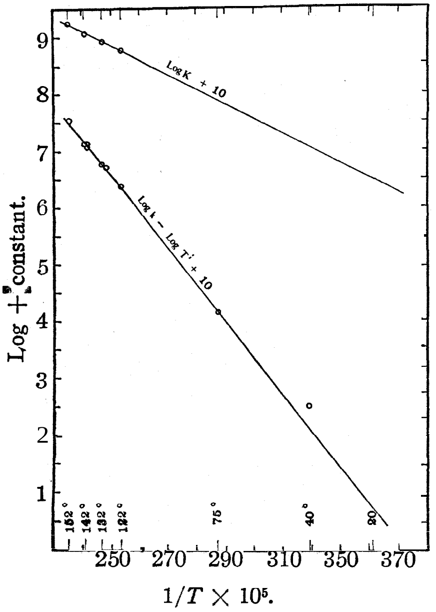


Fig. 3.—Upper line, equilibrium constant (log K + 10); lower line, rate constant (log K_1 − log $T^{1/2}$ + 10).

Experiments with "P" solutions were also performed at higher temperatures (122, 132, 152°, Figs. 1 and 2). In all of these experiments the curves obtained were indistinguishable from straight lines. This is due to the fact that at the higher temperatures the amount of iodine formed during the first several minutes was sufficient to obscure the presence of the side reaction. The existence of the uncatalyzed reaction at the higher temperatures was established in the following manner. Assuming that iodine was formed through the operation of the iodine-catalyzed reaction only, and using the rate equation obtained from measurements with ordinary solutions, it was possible to calculate the amount of iodine that should be present at the time the first sample was taken. In every case it was found that the amount of iodine actually formed was larger than the calculated amount, in spite of the fact that it took from ten to twenty minutes for the temperature inside the bomb to reach the temperature of the thermostat. The difference observed was much larger than the maximum possible experimental error, proving without doubt the existence of a side reaction. However, the accuracy with which this type of measurement could be carried out was not sufficient to throw any light on the nature of the side reaction.

An inspection of Fig. 3 will show that the rate "constant" at 40° as

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[3] In the case of 14-P the objection may be raised that a straight line could be drawn through the points indicated on the plot. However, the curve must pass through the point (not shown on the plot) corresponding to the initial, unknown but very low, iodine concentration.

obtained graphically from Fig. 2 is too high. This is probably due to the fact that, because of the operation of a smaller temperature coefficient, the rate of the side reaction acquires the same order of magnitude as that of the "main" reaction. Experiments with colorless solutions seemed to substantiate this explanation. While the results were not quite decisive, lack of time prevented any further study of these extremely slow reactions.

The Decomposition of the Solid

The decomposition of the solid is catalyzed by iodine. Thus when the unpurified sample was heated it decomposed rapidly at about 45°. The purified iodide gave a sharp melting point at 81.5°. No decomposition took place. The purified substance ground together with some iodine decomposed at 45°. Finally, the purified substance ground together with a neutral powder ($BaSO_4$) gave a sharp melting point at 81.1°, without decomposition.

The Equilibrium Constant

The second product of the decomposition is ethylene. This was manifest from the effect of the reaction mixture on bromine. While quantitative experiments were undertaken, no satisfactory agreement could be obtained between the ethylene content as found from bromination experiments and that calculated from the increase in iodine concentration. However, blank experiments with ethylene solutions in carbon tetrachloride have indicated that the bromine determination is extremely unreliable.

The equilibrium measurements were complicated by the fact that certain slow side reactions were taking place in the equilibrium mixture containing carbon tetrachloride, ethylene iodide, ethylene and iodine. In most of the experiments the "iodine content" increased to a maximum and then decreased very slowly. Blank experiments with pure carbon tetrachloride and with solutions of iodine in carbon tetrachloride have thrown only little light on this phenomenon. However, it was definitely established that the slow decrease in oxidizing agent content was not due to a slow splitting of hydrogen iodide from the ethylene iodide, followed by a recombination of ethylene and iodine to reestablish equilibrium. The amount of hydrogen iodide formed was much too small to account for the total change in iodine content.

With the observed general trend in mind, it was possible to get a satisfactory estimate of the value of the equilibrium constant for four different temperatures. After all the values had been determined they were tested on a log K–$1/T$ plot (Fig. 3) and were found to be fairly well represented by the following empirical equation

$$\text{Log } K_{10} = 4.964 - \frac{2450}{T} = 4.964 - \frac{11300}{2.3RT} \qquad (5)$$

Equation 5 yields a provisional value, 11,300 cal., for the heat of dissociation of EI_2 in carbon tetrachloride solution.

Kinetics of the Reverse Reaction

While the kinetics of the reverse reaction was not studied experimentally, the equation for the rate of formation of ethylene iodide may be derived from theoretical considerations. Thus, if we make the usual assumption that at equilibrium the direct and reverse reactions are taking place simultaneously, we get the following equation for the kinetics of the reverse reaction

$$\mathrm{d}EI_2/\mathrm{d}t = k_2(E)(I_2)^{3/2},$$

where $k_2 = k_1/K$.

Since the values of k_1 and of K have been obtained experimentally, it is possible to calculate the value of k_2 for any temperature. The equation is given in Table II.

Mechanism of the Reaction.—The order of the reaction with respect to iodine suggests the interpretation that the decomposition of EI_2 is catalyzed by free iodine atoms present in "solution. Before we consider this possibility in detail, we may pause to offer another mechanism, of an altogether different nature, yet leading to the same kinetic equation

$$2EI_2 + I_2 = 2EI_3 \text{ (rapid and reversible)} \qquad (6)$$

$$EI_3 = E + I_2 + I \text{ (rate determining step)} \qquad (7)$$

This possibility is of interest in that it does not involve free iodine atoms. It was considered in the preliminary stages of the investigation, when it was thought that the solutions did not contain a sufficient number of free halogen atoms to account for the rate observed. However, since catalysis by free halogen atoms had been observed in several other reactions, and since such an assumption yields itself to a quantitative test, we shall proceed to examine it in the light of the modern theory of bimolecular reactions.

It is possible indeed to formulate several detailed mechanisms involving iodine atoms and leading to the observed kinetic law. However, they are all experimentally indistinguishable from one another and can be represented by the following scheme

$$I_2 = 21 \text{ (reversible)} \qquad (8)$$

$$EI_2 + I = (X) = E + I_2 + I \text{ (rate determining)} \qquad (9)$$

This is a condensed symbolic presentation of the physical process that is taking place and can be elaborated as follows. It is assumed that the decomposition of the ethylene iodide molecule must be preceded by its collision with an iodine atom. While the majority of collisions is elastic, a small fraction results either in the immediate disruption of the molecule or in a series of transformations that leads to the eventual separation of the ethylene group. It is evident that, while the collision between reactant and catalyst is a necessary condition, it is not always a sufficient one; the group, as a whole, must possess a minimum amount of energy before the reaction can take place.

The Energetics of the Reaction

Introduction.—In the discussion that follows, the magnitude of the heat of activation is estimated from the temperature coefficient and is found to be nearly equal to the heat of dissociation of ethylene iodide; the same result is obtained when the heat of activation is estimated from the ratio of the number of effective collisions to the total number of collisions; two analogous reactions, studied by other investigators, are next examined by the same method and are found to yield similar results.

The Heat of Activation.—If the kinetics of the decomposition were represented by the scheme

$$dI_2/dt = k'(EI_2)(I);\ \ \log k' = A' + {}^1/_2 \log T - Q'/2.3RT \tag{10}$$

then the heat of activation, Q', could be obtained directly from the second equation. However, the equations actually used were of the form

$$dI_2/dt = k_1(EI_2)(I_2)^{1/2};\ \log k_1 = A_1 + {}^1/_2 \log T - Q/2.3RT \tag{11}$$

From 10 and 11 it follows that

$$29{,}500 = Q' + Q'' \tag{12}$$

where $2Q''$ is the heat of dissociation of iodine in carbon tetrachloride solution. Although the magnitude of this quantity is unknown, we can use, as a first approximation, the results of Starck and Bodenstein on the dissociation of the gas at high temperatures[4]

Their equation for the equilibrium constant is reproduced here, since it will later be used again for the estimation of the concentration of iodine atoms

$$\text{Log } K_p = 35{,}480/2.3RT + 1.75 \log T = 0.000416T + 0.422 \tag{13}$$

Since these workers investigated the reaction at an average temperature of 1273°K., it is estimated that the heat of dissociation of iodine at 132° is about 33,000 cal., and the heat of formation of a gram-atom of free iodine atoms is 16,500 cal. Substituting this value of Q'' in Equation 12, we find that the heat of activation is equal to 13,000 cal. We have previously found that the heat of dissociation of ethylene iodide is 11,300 cal. (Equation 5). We therefore arrive at the highly interesting result that, within the limits of experimental error, the heat of activation, obtained from kinetic measurements, is equal to the heat of dissociation of the molecule, obtained from equilibrium measurements.

The Heat of Activation from the Number of Effective Collisions.—In a gaseous bimolecular reaction in which the heat of activation, Q', is known, it is possible to predict the rate, provided it is assumed that every colli-

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[4] Starck and Bodenstein, *Z. Elektrochem.*, 16, 961 (1910).

sion in which the joint energy exceeds Q' is effective; for the number of effective collisions, defined as above, is given by the equation[6]

$$\frac{\text{Number of effective collisions}}{\text{Total number of collisions}} = e^{-Q'/RT} \tag{14}$$

and the total number of collisions can be calculated from gas kinetic laws. On the other hand, with the same assumption it is possible to use Equation 13 to calculate Q', if the rate is known. We propose to use this second method to obtain the value of Q' and to compare this value with the one calculated from the temperature coefficient of the rate constant.

It would be surprising indeed to find a bimolecular reaction in which every collision satisfying the energy requirement led to decomposition. However, several cases are known[6] in which the probability factor lies between 1.0 and 10^{-2}. Furthermore, there is no *a priori* reason why the probability factor should be smaller in solution, since we are unable to foretell the effect of the participation of a solvent molecule in a triple collision on the issue of an encounter. We shall proceed, then, to evaluate Q', bearing in mind the approximations involved, as well as the fact that, at the temperature used, a ten-fold error on the left side of Equation 14 introduces an error of 1800 cal. in the magnitude of Q'.[7]

To carry out the computation, we shall assume a solution containing 1.0 equivalent/kg. of EI_2 and 1.0 equivalent/kg. of iodine. With the use of the experimentally observed rate constant we shall determine the speed of iodine formation in such a solution at 142'. We shall also estimate the number of collisions between EI_2 molecules and **I** atoms under those circumstances. The ratio of the two quantities will give us the value of $e^{-Q'/RT}$. In our calculations we shall make use of the following information.

The rate constant at 142° is 2.94 X 10^{-2} e./kg./min. (from Fig. 2). The density of carbon tetrachloride at 142° is 1.42. The number of collisions is given by

$$Z = 10^{28.4427}\,\sigma_{12}^2\sqrt{\frac{M_1+M_2}{M_1M_2}\,T}\,(EI_2)(I) \tag{15}$$

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[5] Cf. C. N. Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, 1926, pp. **53** and **97.**

[6] Hinshelwood, Ref. 6, p. **48.**

[7] It may be worth while to list the errors involved in the two methods of evaluating Q. In the temperature-coefficient calculation the quantity **29,500** was obtained from the slope of the Arrhenius line for the experimentally observed rate constants. The heat of formation of a gram-atom of iodine in carbon tetrachloride solution was estimated from equilibrium measurements on the gaseous phase at very high temperatures. The maximum possible error in Q' was, roughly, **4000** cal.

In the calculation involving the number of collisions, gas laws will be applied for a solution. The degree of dissociation of iodine in carbon tetrachloride will be estimated with the aid of Equation **13,** which was obtained from measurements in the gaseous phase at about **1273** °K. Finally, the assumption will be made that the probability factor is unity. Here, again, the possible error is about **4000** cal.

where Z is the number of moles/cc. suffering collision per second, σ_{12}, is the average diameter, M is the molecular weight, and the concentrations are in moles/cc.[8] The concentration of iodine atoms is calculated by the aid of Equation 13.

Assuming $\sigma_{12}^2 = 10^{-15}$, the results obtained are as follows

$$(EI_2) = (I_2) = 1.0 \text{ e./kg.} = 3.52 \times 10^{-4} \text{ mole/cc.}$$
$$(I) = 6.6 \times 10^{-12} \text{ mole/cc.}$$

Observed rate of iodine formation = 1.72×10^{-7} mole/cc./sec.

Number of collisions = 0.14 mole/cc./sec.

$$e^{-Q'/RT} = (1.72 \times 10^{-7})/0.14; \quad Q' = 11{,}250 \text{ cal.}$$

Collecting the values obtained, we find that the heat of activation as evaluated by the two methods is equal to 13,000 and 11,250, respectively. The heat of dissociation of EI_2 is equal to 11,300 cal. We may conclude that, within the limits of experimental error, the mechanism assumed leads to a satisfactory interpretation of the magnitude of the rate at a single temperature, as well as that of the temperature coefficient.

Similar Reactions

The Decomposition of Phosgene.—The plausibility of the interpretation given in the preceding section is strengthened by evidence from an entirely different source. The decomposition of phosgene, $COCl_2 = CO + Cl_2$, is analogous to that of ethylene iodide, in that in both cases a dihalide breaks up into unsaturated and halogen molecules. Moreover, the kinetics of the reaction was shown to be represented by the equation[9]

$$dCl_2/dt = k(COCl_2)(Cl_2)^{1/2} \text{ (moles/liter/min.), in which}$$
$$\text{Log } k = -11.420/T + 15.54$$

Christiansen suggested two mechanisms, both of which involve chlorine atoms as the catalyst. Bodenstein and Plaut,[10] in their paper on the kinetics of the direct and of the reverse reactions, have estimated that at 668°K. the fraction of collisions that results in decomposition is about 4×10^{-7}.

We can go a step further and, using the ideas developed in the previous section, offer an interpretation of the energetics of the process. The "apparent heat of activation" is $4.57 \times 11{,}420 = 52{,}200$. (At the high temperatures used the effect of omitting the $^1/_2$ log T term in the Arrhenius equation for a bimolecular constant is small.) This is equal to the sum of the heat of formation of a gram-atom of chlorine and of the true heat of activation. Taking the former as 28,000 we arrive at the result that the heat of activation is 24,200. On the other hand, the heat of dissociation of phosgene, as calculated from equilibrium measurements, is 26,000.

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[8] Cf. R. C. Tolman, "Statistical Mechanics," Chemical Catalog Co., New York, 1927, p. 71.

[9] J. A. Christiansen, *Z. physik. Chem.*, **103**, 99 (1922).

[10] Bodenstein and Plaut, *ibid.*, 110, 399 (1924).

It follows that in the decomposition of phosgene, the heat of activation is also roughly equal to the heat of dissociation of the molecule, thus completing the analogy between this reaction and the one under investigation.

When we attempt to estimate Q' from the fraction of fruitful collisions, we have $4 \times 10^{-7} = e^{-Q'/RT}$, and Q' = 19,600. The agreement is not as good, as in the previous calculation. Looked at from another angle, it may mean that the rate observed is about fifty times as large as the theoretical number of effective collisions, calculated with the use of the gas-kinetic formula for the number of collisions. This may be due to two causes. The mean velocity of the "hot" molecule is much larger than the average velocity assumed in the derivation of the formula. Secondly, the effective mean diameter in a "chemical" collision may be larger than that in a "physical" one.[11]

The Decomposition of Ethylene Iodide in the Presence of I^-.—The decomposition of EI_2 in aqueous alcoholic solution was found to be catalyzed by iodide ions.[12] The reaction was found to be of the first order with respect to both reactant and catalyst. The reaction constant at 25° was 0.05 (mole/liter/min.). The temperature quotient was about 2.5.

Here, again, we shall assume that the decomposition takes place after those collisions between EI_2 and I^- molecules in which the energy available is equal to or greater than the heat of activation. Here, too, the heat of activation can be obtained by two methods: from the temperature coefficient of the reaction constant and from the number of effective collisions. The values obtained are 16,800 and 16,200, respectively. While the excellent agreement is fortuitous, since the gas laws for the number of collisions were used for a solution, and the value of σ_{12}^2 was arbitrarily taken as 10^{-15}, still it is believed that the evidence obtained from this, as well as from the other two reactions, points to the fact that there are some elements of reality in the crude picture of the mechanism as proposed in the preceding pages.

Acknowledgment.—The writer wishes to express his appreciation to Professor G. N. Lewis, who suggested this problem and under whose direction the research was carried out, to other members of the staff, and particularly to Professor W. C. Bray for valuable suggestions and advice.

Summary

The statics and kinetics of the autocatalytic decomposition of ethylene iodide in carbon tetrachloride solutions have been investigated. A simple mechanism has been proposed, and with its aid the energetics of the

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[11] *Cf.* Hinshelwood, Ref. 6, p. 63.

[12] A. Slator, *J. Chem. Soc.*, **35**, 1697 (1904).

reaction has been interpreted. (The relations are summarized in Table II.)

TABLE II

SUMMARY OF STATIC AND KINETIC RELATIONS

A. Equilibrium (experimental)

$$11{,}300\text{ cal.} + CH_2I{-}CH_2I \underset{k_2}{\overset{k_1}{\rightleftarrows}} CH_2{=}CH_2 + I_2$$

$$(E)\ (I_2)/(EI_2) + K;\ \log K = -11{,}300/4.57T + \begin{cases} 4.964 \text{ equiv./kg.} \\ 4.663 \text{ moles/kg.} \end{cases}$$

B. Kinetics of the decomposition (experimental)

$$d(I_2)dt = k_1(EI_2)(I_2)^{1/2}$$

$$\text{Log } k_1 = -29{,}500/4.57T + {}^1/_2 \log T + \begin{cases} 12.642 \text{ equiv./kg./min.} \\ 12.793 \text{ moles/kg./min.} \end{cases}$$

C. Kinetics of the reverse reaction (deduced from **A** and B)

$$d(EI_2)/dt = k_2(E)(I_2)^{3/2}$$

$$\text{Log } k_2 = -18{,}200/4.57T + {}^1/_2 \log T + \begin{cases} 7.678 \text{ equiv./kg./min.} \\ 8.130 \text{ moles/kg./min.} \end{cases}$$

D. Values of the constants at 142"

$k_1 = 0.042$ (moles/kg./min.) $k_2 = 0.87$ $K = 0.05$

E. Proposed mechanism of reaction

The decomposition of a molecule must be preceded by its collision with a free iodine atom. Only those collisions are effective in which the energy available is equal to or greater than the heat of activation. The heat of activation cannot be smaller than, and turns out to be approximately equal to, the heat of dissociation of the molecule.

Attention has been called to two analogous reactions that can be interpreted with the aid of the same mechanism.

It has been found that, aside from the main reaction, there takes place *a* slow decomposition which is independent of the iodine concentration.

The decomposition of the solid iodide has been found to be catalyzed by iodine.

BERKELEY, CALIFORNIA

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

THE THERMAL DECOMPOSITION OF HYDRAZINE

BY PHILIP J. ASKEY

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From some experiments performed during an investigation of the photochemical decomposition of hydrazine[1] it appeared that the thermal decomposition in a silica bulb followed a different course from that which resulted from illumination or after activation by excited mercury. With light or excited mercury as a source of activation the hydrazine decomposed to ammonia, nitrogen and hydrogen, according to the equation

$$2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2$$

but from observations of reaction end-points it appeared to decompose thermally to ammonia and nitrogen

$$3N_2H_4 \longrightarrow 4NH_3 + N_2$$

The experiments described below were undertaken as a more extensive study of the nature of the thermal reaction on quartz, and they were compared with a few experiments on the decomposition on heated platinum and tungsten wires. The general conclusions reached were: (1) the decomposition in a silica vessel is heterogeneous, and while it appears primarily to follow the course

$$3N_2H_4 \longrightarrow 4NH_3 + N_2$$

kinetically it is of the first order with respect to hydrazine.

(2) The reaction on heated platinum and tungsten wires follows the course

$$2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2$$

and is of the first order with respect to hydrazine. Hydrogen has a marked retarding effect on the reaction on platinum but practically none in the case of tungsten.

Experimental Method and Discussion of Results

(1) **Decomposition of Hydrazine in a Silica Bulb.**—The course of the reaction was followed by observing the increase of pressure accompanying decomposition and subsequently analyzing the products. Hydrazine is a comparatively high boiling liquid, and if stopcocks are used in the apparatus it is impossible to obtain a reasonable pressure of the substance without condensation at some point. This difficulty was overcome by using in place of stopcocks a form of mercury valve. Two pieces of glass rod had one end ground to fit into correspondingly ground joints in the upper part of a U-bend. Ordinarily, these glass rods rested loosely in the U-bend and there was free communication throughout; but by rais-

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[1] Elgin and Taylor, THIS JOURNAL, 51, 2059 (1929).

ing a mercury leveling bulb the rods were pushed into position by the mercury and formed a gas-tight stop. It was subsequently found advantageous to make the movable part of the joint of tubing filled with iron filings, so that the stop could be broken against a back gas pressure by means of an electromagnet. The whole internal system was kept at about 100° by means of small furnaces and nichrome wire windings. Hydrazine was purified by distilling from barium oxide several times in vacuo, and a small bulb of it was sealed onto the apparatus. The required pressure was obtained by heating the bulb, and the course of the decomposition followed on a constant volume manometer.

The observed order of reaction obtained both from the effect of the initial pressure upon the time of half change, and from the ratio of the times for 50, 75 and 87.5% decomposition in a particular reaction, is approximately equal to one. This is illustrated by the following table.

T, °C.	Initial pressure, mm.	Time for x % decomposition, seconds		
		50	75	87.5
285	153	2940	..	..
298	154	728	1650	3120
298	95.8	639	1275	..
298	78	960	2040	3300
298	24	720		
310	111	384	..	..
310	52	390	840	..
298[a]	109	80	..	..
298[a]	50	128	260	..

[a] Bulb two-thirds filled with silica.

The figures quoted for the reaction bulb two-thirds filled with silica indicate the heterogeneous nature of the reaction, the reaction rate being increased nearly ten times.

In the next table the final increase of pressure, that is, the "end-point" pressure, is given for a number of reactions. If the decomposition was

$$3N_2H_4 \longrightarrow 4NH_3 + N_2$$

the increase of pressure would be 66.6% of the initial pressure; while if it was

$$2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2$$

it would be a 100% increase of pressure.

Temperature, °C.	271	276	298	298	298	298	298	298	310	298"
Init. press., mm.	30	120	154	98.5	85	78	24	21.8	52	50
Tot. press. incr., mm.	17.5	90	102	61	50	52	17	13	31	31.8
% press. increase	58	74	66	62	59	67	71	60	60	64

[a] With silica packing.

These figures show that $3N_2H_4 \longrightarrow 4NH_3 + N_2$ represents the course of the reaction; this was confirmed by analysis of the products.

Analysis.—A portion of the gaseous products was withdrawn into a gas holder and its pressure measured when occupying a certain volume. It was then circulated (1) through a tube cooled in solid carbon dioxide and ether, (2) through a tube cooled in liquid air, and the diminution of pressure after each operation was noted. The former gave the amount of residual hydrazine, if any, and the latter the amount of amfnonia. The residual gas was circulated through a tube of cupric oxide heated to 300° when the hydrogen was burned to water. This was condensed by carbon dioxide and ether, and the diminution of pressure gave the amount of hydrogen. The residue was assumed to be nitrogen.

Temp., °C.	Init. press., mm.	Press. incr., mm.	Products, mm.	Residual N_2H_4, mm.	NH_3, mm.	H_2, mm.	N_2, mm.
271	30	17.5	29	2	17	2.5	7
298	44.5	25	47	6	26	2.5	10

In each analysis a small amount of hydrogen was found, indicating that part of the reaction is going $2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2$, but it is insufficient noticeably to affect the end-point pressures.

(2) Decomposition of Hydrazine on a Heated Platinum Wire.—The reaction vessel was spherical with a capacity of about 150 cc., and had a platinum filament with tungsten leads through the glass. Electrical energy was supplied by two storage batteries, and was measured by an ammeter and voltmeter and controlled by finely adjustable resistances. Since the thermal conductivity of the gas changed during the course of an experiment, it was necessary continuously to adjust the resistances, so that the ratio of the voltage to the amperage, and hence the resistance of the wire, remained the same. This insured a constant temperature. The temperature–resistance curve of a piece of the same platinum wire was obtained by measurements in a furnace, the temperature of which was known by means of a calibrated thermocouple. Hence the temperature of the filament could be determined, a 5% correction being made for loss of heat by the heavier tungsten leads. Pressures were read on a constant column mercury manometer and the reaction vessel was kept in a water-bath at 25°.

Hydrogen has a strong retarding influence on the decomposition of the hydrazine. This appears both from the rapid initial reaction followed by a falling off in the rate as the products accumulate, and from the inhibition of the reaction when hydrogen is added beforehand. The first point is shown by the following experiment.

INITIAL PRESSURE OF HYDRAZINE, 11 MM.; TEMPERATURE, 205°

Time, minutes	1	2	5	10	15	20	30	40	70	110
Pressure increase, mm.	3	4	5.5	6.7	8	9.6	10.4	11	11.8	12

Nitrogen has considerably less effect than hydrogen in slowing down the reaction. The following comparative reactions with hydrogen and nitrogen illustrate this point.

Temp., °C.	Initial press., mm N_2H_4	H_2	N_2	Time for x % decomposition, minutes 10	20	50	75
205	11	...	...	..	1	5	13
205	7.5	5.5	...	89	...	255	..
205	8	...	13.5	..	1.5	12	30

In another experiment a mixture of 11 mm. of hydrazine and 12 mm. of hydrogen which decomposed extremely slowly at 205°, when heated to 500° decomposed completely in forty minutes.

The effect is very similar to that found for the thermal decomposition of ammonia by Hinshelwood and Burk.[2]

The course of the reaction follows the equation

$$2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2$$

as shown by observations of the end-points of the reaction, and by analysis of the products as described above. As we are dealing here with smaller pressures of gas, the results are less accurate than could be desired, but are sufficient to confirm the nature of the reaction.

Temperature, °C.	173	267.5	205	375	450	530	205
Init. press. N_2H_4, mm.	8.2	8	11	7	10	11 (H_2, 12)	8 (N_2, 13.5)
Final press. incr., %	96	90	109	105	110	112	125

RESULTS OF ANALYSES

Temp., °C.	Total products, mm.	N_2H_4, mm.	NH_3, mm.	H_2, mm.	N_2, mm.
260	16.7	0	8.7	...	...
205	15	0.4	6.4	3.4	4.8
267.5	15.2	1 2	7.8	2.0	4.2
205	23	0	13	4	6

(3) The Decomposition of Hydrazine on a Tungsten Wire.—The experimental method was the same as for the reaction on platinum. The reaction is not retarded by the presence of excess hydrogen as in the case of the reaction on a platinum filament. On the contrary, it was even accelerated somewhat, but this might have been due to errors in controlling the temperature.

Temp., °C.	Init. press, mm. N_2H_4	H_2	Time for x % decomposition, minutes 10	20	40	50	75
380	9	..	2	5	16	26	65
360	8	8	1.5	4	10	13	27.5
380	7	14	1	2	6	10	..

Considering the course of an individual decomposition, it would appear to be approximately of the first order. The hydrazine decomposes to ammonia, nitrogen and hydrogen, as on platinum. This is illustrated by the following experimental end-points.

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[2] Hinshelwood and Burk, J. *Chem. Soc.*, 127, 1105 (1925).

Temperature, °C.	600	450	360	380	380
Init. press. N_2H_4, mm.	7.5	9.5	8	9	9
Init. press. H_2, mm.	...	...	8	...	14
Tot. press. incr., %	93	106	98	91	93

The measurement of the temperatures of filaments in the manner described above is not particularly accurate, but it is clear that at temperatures approximately close to each other hydrazine decomposes on tungsten and platinum in a manner quite different from that which it follows on quartz, but similar to that which obtains in the presence of excited mercury and on illumination. For this singular behavior on quartz we can at present offer no explanation. It might be pointed out that the discrepancy between the pressures used in the quartz and filament reactions is of no significance, because Elgin, when he first noticed the reaction on quartz, was using pressures of 8 to 10 mm.

In conclusion, we should like to state that we have been enabled to carry out this work thanks to a Procter Visiting Fellowship at Princeton. We should also like to express our appreciation of the advice and helpful suggestions we have received from Professor Hugh S. Taylor.

Summary

The thermal decomposition of hydrazine on quartz and also on platinum and tungsten wires has been studied. On quartz the reaction follows the course $3N_2H_4 \longrightarrow 4NH_3 + N_2$, while on platinum or tungsten it follows the course $2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2$.

PRINCETON, NEW JERSEY

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

THE OXIDATION OF BENZALDEHYDE AND FORMALDEHYDE IN THE GASEOUS PHASE

BY PHILIP J. ASKEY

RECEIVED NOVEMBER 8, 1929 PUBLISHED MARCH 0, 1930

Recently it has been observed that a number of oxidations in the gaseous phase appear to be chain reactions. This is true of the vapor-phase oxidations of phosphorus,[1] of the homogeneous reaction of hydrogen and oxygen,[2] of the oxidation of propane and the butanes,[3] and of several other reactions. The chief characteristic of such reactions is the suppression of the rate of oxidation when the reaction vessel is packed with material of the same nature as itself, and this inhibiting effect is enhanced when the quartz or glass packing is coated with some inert substance like potassium chloride.

[1] Semenoff, *Z. Physik*, 46, 109 (1927).

[2] Hinshelwood, *Proc. Roy. Soc. London*, 118A, 170 (1928).

[3] Pease, THIS JOURNAL, 51, 1839 (1929).

At the same time, several oxidation reactions in the liquid phase, both thermal and photochemical, have been shown to be chain reactions[4] The work of Engler, Bach and others had indicated that in a number of autoxidation processes there is intermediate formation of peroxide bodies which then react further with the original substance, and in **his** investigation of the liquid phase oxidation of benzaldehyde, Bäckström[4b] demonstrated conclusively that benzoperacid was an intermediate product and subsequently reacted with further aldehyde. In addition to this he showed that it was the reaction resulting in the formation of the benzoperacid which gave rise to the activation necessary for the continuity of the chain. From work that has been done by Gill, Mardles and Tett[5] and by Pope, Dykstra and Edgar,[6] as well as by Pease,[3] it appears not only that aldehydes are intermediate products in the oxidation of various hydrocarbons, but also that they exhibit, when oxidized themselves, characteristics such as luminescence and sensitiveness to inhibition which are typical of chain reactions. Pease, therefore, concludes that the aldehyde oxidation is the basis of his chain mechanism for the oxidation of hydrocarbons. It should, however, be pointed out that Gill, Mardles and Tett[5] in studying the oxidation of hexane, came to the conclusion that the luminescence was due not to the intermediate formation of aldehydes but to the formation of primary peroxides of hexane.

In this paper we wish to present the results of a few preliminary experiments on the oxidation of benzaldehyde and formaldehyde in the vapor state. These experiments, while they do not provide a detailed and intimate picture of the mechanism of the oxidation process, at least indicate a few significant features. In the first place, they indicate that both oxidation processes are chain reactions, characterized by a considerable suppression of the rate when the reaction bulb is packed with quartz; secondly, that in the case of benzaldehyde, oxygen itself acts as an inhibitor when present in excess. There also appears evidence that there is a slight induction period in the oxidation of benzaldehyde, while none was apparent in the oxidation of formaldehyde.

The oxidation of benzaldehyde proceeds at about 200°; that of formaldehyde at about 330°.

Experimental Method

The method used was the same for both benzaldehyde and formaldehyde. The oxidation was carried out in a quartz bulb of about 200-cc. capacity heated in an electric furnace, the temperature of which was measured by means of a thermocouple. All the external connections of the apparatus

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[4] (a) Backstrorn, THIS JOURNAL, 49, 460 (1927); (b) *Medd. Vetenskapsakad. Nobelinst.*, *6*, *No.* 15; (c) *6*, No. 16.

[5] Gill, Mardles and Tett, *Trans. Faraday Soc.*, *24*, 575 (1928).

[6] Pope, Dykstra and Edgar, THIS JOURNAL, 51,1875 (1929).

were wound with nichrome wire and maintained at about 100°. Stopcocks were dispensed with and mercury operated vaives, which could be heated to 100°, were substituted.

Freshly distilled benzaldehyde or paraformaldehyde was contained in small bulbs sealed onto the apparatus, and the required pressure of aldehyde was obtained by heating the bulb. It was then shut off from the reaction vessel. Oxygen was admitted from a gas holder and the course of the reaction was followed by the pressure change indicated by a constant volume manometer.

For the reactions in a packed bulb the latter was filled with coarse quartz grains which had been carefully cleaned with nitric acid, washed and dried.

In one or two experiments with benzaldehyde a rough attempt was made to analyze some of the products of reaction. These were withdrawn into a gas holder through a U-tube cooled in solid carbon dioxide and ether. This, presumably, condensed out all but carbon dioxide, carbon monoxide and permanent gases. The residue was then passed through liquid air to remove any carbon dioxide, and the diminution of pressure was noted. The fraction condensed out with solid carbon dioxide and ether was distilled into another vessel and examined, but the quantity of material was so minute that little information could be obtained.

Discussion of Results

(1) **Benzaldehyde.**—A series of experiments was carried out at a temperature of 198° with different initial pressures of benzaldehyde and oxygen. It has been assumed that the final product of the oxidation would be benzoic acid

$$2C_6H_5CHO + O_2 \longrightarrow 2C_6H_5COOH$$

and that there would be a final decrease in pressure equal to half the initial pressure of benzaldehyde. It was found that this was only true when the initial pressure of oxygen was almost double that required by the above equation. When the proportion of oxygen was less than this, the reaction, although it went at a greater rate than when more oxygen was present, stopped short at a point which would have appeared to indicate incomplete oxidation. We shall return to the explanation of this later. In every reaction there was a final increase of pressure of one or two millimeters; due possibly to a slow decomposition of the products.

In the following table are given the final pressure decrease and the times taken to reach this pressure by mixtures of benzaldehyde and oxygen in different proportions.

TEMPERATURE, 198°C.

Initial pressures, mm.	Benzaldehyde	38	30	33	30	23
	Oxygen	24	20	21	28	32
Final pressure decrease; mm.		12.8	10	10	13	10.5
Time to reach final press. decr., min.		18	16	32	91	91

By "final pressure decrease" we mean the maximum pressure decrease reached before the subsequently slow and comparatively small pressure increase.

The following table shows the difference in the rate of oxidation in an empty bulb and a packed bulb.

Bulb	Temp. °C.	Initial pressure, mm. Benzaldehyde	Initial pressure, mm. Oxygen	Time taken to reach x % of final pressure decrease, minutes 10	20	30	40	50	60	70	80	90	100
Empty	198	38	24					13					
Empty	198	23	32	8	16	21		36			55		91
Empty	198	30	20	3		5		7		10			16
Empty	198	33	21		4.5			11		14	19		32
Empty	198	30	28		14			34			54		81
Packed	198	34.5	25			300			1440				5760
Packed	198	35	47					Very slow					
Empty	224	30.5	26			1				4			7
Packed	224	30.5	24.5		120								800
Empty	242	36	85					Very slow					

A complete investigation should, of course, include the influence of other gases on the reaction, and also the result of a wider variation of the initial pressures of benzaldehyde and oxygen. It is, however, quite clear that the oxidation of benzaldehyde exhibits the main characteristics of a chain reaction—the suppression of the rate in a packed bulb. The above experiments also show the inhibiting effect of excess oxygen, and in this respect parallel the observations of Pease on the oxidation of propane and the butanes.

The mechanism of the chain propagation is still somewhat of a moot point, although it seems most likely, by analogy with other oxidations and particularly that of benzaldehyde in the liquid phase, that benzoperacid is the first product of oxidation, subsequently reacting with a further molecule of benzaldehyde

$$C_6H_5CHO + O_2 \longrightarrow C_6H_5COOOH \qquad (1)$$

$$C_6H_5COOOH + C_6H_5CHO \longrightarrow 2C_6H_5COOH \qquad (2)$$

The question then arises as to which of these reactions is responsible for the activation of another molecule of benzaldehyde and the continuance of the chain. In the liquid-phase oxidation, Backstrom showed that it was the first reaction which was primarily responsible for further activation. At the same time he showed that there is no reason why the reaction between the peracid and aldehyde should not cause activation of other molecules, but to a much smaller extent, which would then react both with oxygen and with benzoperacid. This makes the benzaldehyde the active principle in chain propagation.

An alternative view is that the oxygen is the reactant activated by collision, the oxygen acting as a promoter of the chain

$$A + O_2 \longrightarrow AO_2'$$
$$AO_2' + O_2 \longrightarrow AO_2 + O_2'$$
$$A + O_2' \longrightarrow AO_2'$$

but if we compare the reaction rate for a mixture of **30** mm. of benzaldehyde and **20** mm. of oxygen with that for a mixture of **23** mm. and **32** mm., respectively, it seems fairly clear that it must be the benzaldehyde which is promoting the chain, while the oxygen acts as an inhibitor by breaking the chain in the same way as collision with the wall breaks it, *i. e.*, by taking up the energy of activation, and acting as a carrier of this energy to the wall. Moreover, the former mechanism more readily explains the autocatalytic effect which is observed in this and other oxidatons and which is illustrated by the following data.

TEMPERATURE 198°

(1) Initial pressures: benzaldehyde, 23 mm.; oxygen, 32 mm.

Time, minutes	0	3	8	15	20
Pressure decrease, mm.	0	0	1	2	3

(2) Initial pressures: benzaldehyde, 30 mm.; oxygen, 28 mm.

Time, minutes	0	2	10	20	30
Pressure decrease, mm.	0	0	1.2	8.2	5.3

We may return now to the fact stated above, that in reactions involving smaller proportions of oxygen, the oxidation, although proceeding at a faster rate, did not give the final pressure increase corresponding to complete oxidation to benzoic acid. In one or two experiments the gaseous products were analyzed for carbon dioxide as described above. It was observed that in the reactions involving a high proportion of oxygen there was practically no carbon dioxide formed; but that in those involving a lower proportion of oxygen, carbon dioxide was present in amount approximately equal to the apparent deficiency of oxidation. Thus in the reaction in which the initial pressures of benzaldehyde and oxygen were **33** mm. and 21 mm., respectively, and in which the maximum pressure decrease was 10 mm., there was approximately 6 mm. of carbon dioxide; while in a reaction in which the initial pressures were 30 mm. and 28 mm., respectively, and the maximum pressure decrease was 13 mm., there was only about 2 mm. of carbon dioxide. It was thought that possibly in the reaction involving a smaller proportion of oxygen some of the benzoperacid decomposed to phenol and carbon dioxide, but an attempt to detect phenol in the products of reaction was unsuccessful. Moreover, Erlenmeyer[7] showed that benzoperacid on heating yielded only minute traces of carbon dioxide, decomposing instead to benzoic acid and oxygen. A possible alternative is that the carbon dioxide arises from decomposition of the benzoic acid in an activated state.

[7] Erlenmeyer, Helv. *Chim. Acta,* 10,620 (1927).

The temperature coefficient of the reaction as it stands is fairly high; but this is no measure of the temperature coefficient of the simple bimolecular reaction between benzaldehyde and oxygen. This might possibly be measured in two ways: (1) in the presence of excess oxygen, or (2) in a bulb packed with very fine silica and at low pressures. In either method it is conceivable that the chains would be broken as soon as they were started, and only the primary reactions would have effect.

(2) Oxidation of Formaldehyde.—There are three possibilities for the oxidation of formaldehyde

$$HCHO + O \longrightarrow H_2O + CO \qquad (1)$$
$$HCHO + O \longrightarrow H_2 + CO_2 \qquad (2)$$
$$HCHO + O_2 \longrightarrow H_2O + CO_2 \qquad (3)$$

The pressure increase corresponding to Reactions 1 and 2 would be half the initial pressure of formaldehyde, while (3) would show no change. In the temperature range 320 to 340°, the final pressure increase was not far short of the value corresponding to (1) or (2), but at higher temperatures the pressure increase became less and at 380° was only about one-half the value given by (I) or (2). It seems that either (1) or (2) and *(3)* can occur simultaneously, (3) having the higher temperature coefficient. Gas analyses to distinguish between (1) and (2) were not made.

A few reactions were carried out to determine whether the reaction was suppressed when carried out in a packed bulb, and the results are given in the following table.

Bulb	Temp., °C.	Initial press., mm. HCHO	Initial press., mm. O_2	Time for x % reaction, minutes 10	20	30	40	50	60	70	80
Empty	321	48	40	3		10		36			
Empty	321	41	22					23			
Packed	321	49	45		350			1380			
Packed	321	53	59		600		1500				
Empty	346	47	36.5	1			1	5	10	15	36
Empty	346	48	38				5	5	9	17	36
Packed	346	44	40		240	480					

In the next table is shown the variation of the final pressure increase with temperature.

Temperature, °C.		321	346	370	370	400
Initial press., mm.	HCHO	44	48	48	42.5	47.5
	O_2	40	38	63	36	47
Final press., mm.		20.5	22	12.8	10	6 (approx.)

These experiments are far from exhaustive, but they indicate that the oxidation of formaldehyde has a chain mechanism similar to that discussed in the previous part of the paper.

In conclusion we should like to express our appreciation of the very kind and helpful suggestions we have received from Professor Hugh S.

Taylor, from Dr. Hans L. J. Bäckström and from Dr. R. N. Pease. We should also like to state that we are indebted to a Procter Visiting Fellowship at Princeton for assistance in carrying out this work.

Summary

The thermal oxidations of benzaldehyde and formaldehyde in the vapor phase have been investigated. It has been shown that they are both chain reactions, judged by the characteristic suppression of the rate of oxidation when it is carried out in a packed vessel. The mechanism of the benzaldehyde oxidation is discussed.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SOUTH CAROLINA FOOD RESEARCH COMMISSION AND THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, UNIVERSITY OF MINNESOTA MEDICAL SCHOOL]

THE DETERMINATION OF TRACES OF IODINE. IV. IODINE IN SMALL QUANTITIES OF THYROID AND OTHER TISSUES[1]

BY ROE E. REMINGTON, J. F. MCCLENDON, HARRY VON KOLNITZ AND F. BARTOW CULP

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The tube furnace method originated by one of us[2] for the destruction of organic matter in the estimation of traces of iodine has been modified and adapted to the analysis of thyroid and other glands, oysters and other animal tissues relatively high in iodine. It possesses advantages of brevity and accuracy which make it preferable to any other method which has been described. Other workers have destroyed organic matter in thyroid by fusion with sodium hydroxide, or with sodium hydroxide and potassium nitrate[3] or a carbonate mixture. It has also been done by digestion with sulfuric acid and hydrogen peroxide.[4] All of these processes are time consuming and open to the possibility of loss.

We have found[5] that vegetables can be ignited in a muffle at 450° or less without material loss of iodine but if the temperature is raised to 550° the results are usually low. On dried thyroids, alone or with the addition of calcium oxide or sodium hydroxide, the low-temperature method is not satisfactory. If 0.1 g. of dried thyroid is mixed with 100 g. of dried potatoes, the iodine can be recovered with a fair degree of accuracy, but requires from twelve to twenty-four hours in the muffle and previous careful analysis of the potatoes.

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[1] Presented before the Division of Biological Chemistry at the 78th meeting of the American Chemical Society, Minneapolis, Minnesota, September 9–13, 1929.

[2] J. F. McClendon, THIS JOURNAL, 50, 1093 (1928).

[3] E. C. Kendall, *J. Biol. Chem.*, *43*, 149 (1920).

[4] G. Pfeiffer, *Biochem. Z.*, 195, 128 (1928); E. Glimm and J. Isenbruch, *ibid*, 207, 368 (1929).

[5] J. F. McClendon and R. E. Remington, THIS JOURNAL, 51, 395 (1929).

When we tried to burn powdered thyroid in the tube furnace with the original technique of heat under the tube, most of the material underwent dry distillation. We then tried heating the material by means of a miniature oxygen–gas torch made by soldering together two ordinary laboratory blowpipes. On the powder alone this also caused too rapid burning, and the appearance of tarry matter in the absorption bottles. We next tried diluting the thyroid powder with an excess of inert material, using for this purpose calcium oxide, sodium hydroxide, calcium carbonate, sodium carbonate and sand. Calcium oxide was found most satisfactory if fat had been previously extracted from the thyroid, but if any fat is present, traces of fatty acids may distil onto the sides of the tube and by their effect on surface tension interfere later with the removal of the lime by centrifuging. Acid-washed and ignited sand is very satisfactory for such samples. The subsequent treatment of the ash residue and liquids from the absorption jars is the same as previously described, except that a small amount of sodium azide is used as recommended by Reith,[6] to reduce any nitrites which may be produced in the burning of protein in oxygen. It was found that the iodine from 0.01 g. of thyroid powder could be determined easily colorimetrically when shaken out in 1 cc. of carbon tetrachloride. (The lower limit of accuracy with the Bausch and Lomb micro-calorimeter is probably about 0.01 milligram of iodine for most observers. This amount is contained in 5 milligrams of thyroid powder of 0.2% iodine content.) However, when abundance of material is at hand, greater accuracy in sampling and weighing is obtained by using 0.1 to 0.2 g. of the powder and shaking out the iodine from one-fifth of the final solution. The size of the combustion apparatus has been very much reduced and side-neck test-tubes substituted for the various wash bottles of the original set-up. The combustion can be completed in about five minutes, using a Richards or other water-operated suction pump, and the washing up of the apparatus does not take more than ten minutes. The complete set-up (Fig. 1) is as follows.

The pyrex combustion tube is 210 mm. long and of *25* mm. bore, with a right-angled outlet tube **155** mm. long and of **5** mm. bore. The outlet leads into a side-neck pyrex test-tube **150** mm. long and of 15 mm. bore. Prom the side neck a rubber connection joins the tube with two test-tubes set in parallel by means of a Y-tube. These test-tubes are fitted as gas wash bottles with **3-mm.** bore tubing, the inlet tubes being drawn into capillaries. The gas stream is united again by another Y-tube and leads into the bottom of a large soda lime tube **235** mm. high and of **20** mm. bore, set vertically. This tube has a small porcelain filter disk in the bottom of the bulb and is nearly filled with fine glass wool. **A** tube from the top leading to a suction flask connected with a suction pump completes the set-tip. The three test-tube wash bottles are filled and the glass wool is moistened with a very weak solution of sodium sulfite. The wash bottles

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[6] J. F. Reith, "De Micro-Jodiumbepaling in Natuurlijka Grondstoffen," Dissertation, University of Utrecht, 1929.

are immersed in ice water There is a screw clamp set on the rubber connection below the tower which is used to regulate the suction and to keep the solution in the tower from flowing back into the wash bottles. The two blowpipes forming the torch are soldered together at their centers and the tips may be filed slightly on the inside so as to bring them nearer together. (Hoke, Incorporated, have recently made for us a miniature oxygen--gas torch with a special outlet tube, which is very satisfactory.) The bent end is only about 1 cm. long, so as to give the maximum clearance. Ordinary illuminating gas is used in the lower pipe while oxygen is used in the upper. The combustion boat is of nickel, one end being cut away to admit the torch. It is about 1.5–2.0 cm. wide, 4.0–5.0 cm long and 1 cm. deep.

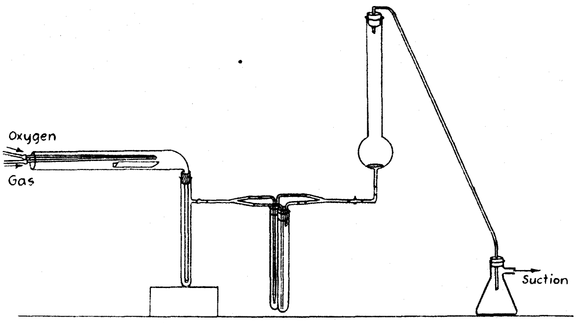

Fig. 1.

Manipulation

The fresh thyroids are weighed, cut into bits and dried at 100° for 24 hours for a rough moisture determination. The resulting glassy mass is ground and a second moisture determination made. Fat is then extracted with anhydrous ether in a Bailey-Walker apparatus.

Approximately 0.1 g. of the powder is accurately weighed into the nickel boat, mixed with about twice its volume of freshly ignited calcium oxide, by means of a platinum wire, and finally covered with a thin layer of the lime, so that no thyroid material can be seen on top. The boat is inserted into the combustion tube until it is about 4 cm. from the inner end of the tube, and the suction regulated by the screw clamp until there is a steady flow which does not draw any solution into the next receiver.

The torch should be so adjusted that the flame will be non-luminous throughout and yet of a force insufficient to blow any material from the boat. An excess of oxygen is used. The sample should be burned slowly, manipulating the torch by hand, starting at the far end of the boat and working toward the rear. (A pair of smoked glasses will be a very great help in watching the combustion.) After the first burning, the mass is stirred or turned over with a platinum wire, so as to expose and re-burn any black spots which remain. This may be repeated if there is further black residue. The entire burning can be completed in five minutes, and the solutions in the absorbers should be perfectly clear and colorless.

The receivers and combustion tube are rinsed into a 250-cc. beaker and the boat with its residue is placed in the beaker. The tube can be more easily washed if some alcohol is used first. The washing of the tower is easily done by connecting the suction flask to the lower outlet and washing the glass wool by gentle suction. The contents and washings of the entire apparatus should not exceed 225 cc.

This volume is evaporated down to about 50 cc., centrifuged from insoluble lime and evaporated to small volume. It is then transferred to a nickel or platinum boat and the evaporation continued to complete dryness. About **0.5** g. of powdered sodium hydroxide is sprinkled over the residue, the boat placed in a combustion tube like the one formerly used and heated by a flame beneath the tube until the hydroxide is completely fused; meanwhile a slow current of air is drawn through the tube and a single absorption tube. This method of fusing with alkali is no more troublesome than fusion in an open dish, and avoids the dangers of overheating and loss of iodine.

The flux is allowed to cool, dissolved in a small amount of water and transferred with the liquid from the absorber and the rinsings of the tube to a 60-cc. beaker. A few mg. of sodium azide is added, the solution made just acid to brom phenol blue paper with sirupy phosphoric acid and **5–10** drops added in excess followed by **5** drops of 8% sulfurous acid. The indicator paper must not be dipped into the solution, but a tiny drop removed on a small rod for the test. It is then heated until the odor of hydrazoic acid disappears, cooled, transferred to a **50-cc.** volumetric flask, made to mark and **10** cc. removed to a small separatory funnel for the colorimetric estimation of iodine as previously described.[2]

TABLE I

ANALYTICAL RESULTS

	Weight taken, g.	Iodine recovered. %		Weight taken, g.	Iodine recovered, %
Thyroid powder	**0.0925**	**0.181**	Anterior pituitary	**0.1589**	**0.0149**
(U. S. P. Lilly)	.4325	.185	(Armour)	.1906	.0126
	.1225	.185		.1914	.0134
	.1232	.179		.2056	.0135
	.1105	.188		.2269	.0130
	.1695	.182			———
	,0897	.186		Av.	.0135
	———	———	Salamander thyroids[a]		
	Av.	.184	(dry weight)	.0262	.342
Oysters, dry basis,	**8540**	.00162	Salamander back		
Charleston Co., S. C.	.7772	.00154	muscle[a] (dry weight)	.0618	.0068

[a] We are indebted to Dr. E. Uhlenhuth of the University of Maryland for the salamander tissues.

TABLE II

HUMAN THYROIDS[a] FROM CHARLESTON, SOUTH CAROLINA

No.	Sex	Age	Weight of entire gland, g.	Cause of death	Iodine in dry fat-free material, %	Iodine in total gland, mg.
8557	F	**35**	**15**	Pellagra	**0.153**	**6.66**
8598	F	**2.5**	**6**	Malaria	.083	**0.73**
8604	**M**	26	**13**	Head injury	.202	**7.12**
8619	M	**38**	**16**	Syphilitic ulcer of duodenum and obstruction	.295	**12.90**
8628	M	**38**	**14**	Myelogenous leukemia	.160	**4.75**
8633	M	**50**	35	General arteriosclerosis	.101	**6.34**
8635	F	**50**	**13**	Syphilitic encephalitis	.264	**8.84**
8669	M	**14**	**10**	Suppurative appendicitis and peritonitis	**,069**	**1.63**
8670	M	**65**	**12**	Acute purulent meningitis	.192	**5.54**
8672	**F**	..	**16**	Suppurative appendicitis and peritonitis	.123	**4.53**
8686	**M**	**78**	**10**	General arteriosclerosis	.280	**6.01**
8706	**F**	**16**	**13**	Acute suppurative pyelo-nephritis	.333	**10.07**
8719	**F**	**38**	..	Stab wound of chest	.200	....

TABLE II (*Concluded*)

No.	Sex	Age	Weight of entire gland, g.	Cause of death	Iodine in dry fat-free material, %	Iodine in total gland, mg.
8732	M	32	14	Arterio-capillary sclerosis	.594	23.70
8733	M	28	16	Not definitely determined	.201	6.75
8745	F	35	..	Arterio-capillary fibrosis	327	10.00
8757	M	28	11	Intestinal obstruction	.229	6 24
8762	..	..	1.5	New-born	061	0.22
X769	F	80	18	Arterio-capillary sclerosis	447	19.2
8787	M	33	16	Syphilitic hemorrhagic pachy-meningitis	203	7.89
8800	F	70	15	General arteriosclerosis	167	5.12
8820	M	17	20	Stab wound and hemorrhage	.304	20.9
8865	..	..	1.5	Infant	.070	0.195
8888	..	..	1.8	Infant	.020	0.065
8894	..	2	2	Tuberculosis	.109	0.423
8898	M	70	15 5	Pulmonary tuberculosis	.275	9.70
8910	..	..	2	Infant	.026	0.118
8916	M	55	26	Syphilitic encephalitis	.163	11.15
8922	F	26	13	Stab wound of chest and heart	.133	3.67
8941	F	30	16	Acute suppurative pyelo-nephritis	.135	4.33
8942	M	32	19	Gun shot wound, abdomen and peritonitis	.210	8.36
8961	F	50	13	Diabetes mellitus	.172	4.95
9058	F	50	21	Lobar pneumonia	.194	7.81
9076	M	35	17	Peritonitis	.259	10.65
9245	F	38	19.1	Not clearly determined	.233	11.67
9256	M	47	14.6	Not determined	.280	6.92
9260	M	27	17.5	Cardiac failure	.087	2.49

[a] We are indebted to Drs. Kenneth M. Lynch and H. H. Plowden of the Department of Pathology, Medical College of the State of South Carolina, for the material and pathological data.

If the quantity of iodine is low, or it is desired to use smaller samples, the entire solution may be boiled down to 5–8 cc. before acidifying, all transferred to the separatory funnel and made up to 10 cc. We have been able to determine iodine in 50 mg. of fresh salamander thyroid, in 0.15 g. of dried anterior pituitary and in 0.75 g. of dried oysters by this method. A sample of desiccated thyroid examined by Kendall's method gave duplicate values of 0.182 and 0.186%, after correcting for blank tests on the reagents. Seven determinations by our method gave values ranging from 0.179 to 0.188% with an average of 0.184. Some typical results are given in Table I. Results on 37 human thyroids from a non-goitrous region (Charleston, S. C.), are given in Table II.

Summary

A micro-modification of the McClendon tube furnace method for iodine estimation has been developed which is applicable to small quantities of biological materials such as thyroid and other glands oysters and other sea food. Aside from the reduced size of the apparatus, the essential modifications are the use of an oxygen–gas torch to burn the sample and the use of lime to retard the combustion and alkalinize the ash, Results are given on thyroid, pituitary, oysters and a series of 37 human thyroids.

CHARLESTON, SOUTH CAROLINA
MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 244]

THE EQUILIBRIUM BETWEEN BIVALENT AND QUADRIVALENT PALLADIUM AND CHLORINE IN HYDROCHLORIC ACID SOLUTION

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Introduction

The equilibrium between palladous and palladic chlorides and chlorine in hydrochloric acid solution seems not to have been previously measured, and no physico-chemical studies have been made as to the state in which bivalent and quadrivalent palladium exist in chloride solutions. It is well known, however, that from such solutions salts of the types R_2PdCl_4 and R_2PdCl_6 separate, and it is probable that in such solutions the palladium exists mainly or wholly in the form of the corresponding ions $PdCl_4^{--}$ and $PdCl_6^{--}$. In that case the equilibrium to be here considered would be expressed by the simple equation: $PdCl_4^{--} + Cl_2 = PdCl_6^{--}$.

It was necessary, however, to consider the possible existence of trivalent palladium in the solution, for complex salts of this valence have been prepared.[1] Therefore, it was thought advisable in some of the experiments to fix the concentration of quadrivalent palladium by saturating the solutions with the slightly soluble potassium chloropalladate (K_2PdCl_6), and to estimate the concentration of trivalent palladium in these solutions by determining the total oxidizing chlorine. Accordingly, one of the steps in this investigation consisted in determining the solubility of potassium chloropalladate. Solutions of palladous chloride in normal hydrochloric acid containing known amounts of potassium chloride were saturated with chlorine at atmospheric pressure, whereby all of the palladium is oxidized to the quadrivalent state. The solubilities of potassium

[1] Wohler and Martin, *Z. anorg. Chem.*, 57, 398–413 (1907), by treating the hydrochloric acid solution of palladous chloride with cesium and rubidium chlorides and chlorine, prepared the compounds Cs_2PdCl_5 and Rb_2PdCl_5, which they found to be more unstable than the corresponding quadrivalent compounds. They failed to prepare K_2PdCl_5 by this method, but with considerable difficulty they obtained some of this compound by treating the oxide, Pd_2O_3 (formed at the anode in electrolyzing palladous nitrate), with potassium chloride and dry hydrogen chloride in ether.

chloropalladate in these solutions were then found by gravimetric determination of the total palladium.

A series of measurements of the equilibrium of the oxidation reaction was made, first in the presence of potassium chloropalladate. The solutions were saturated both with chlorine at some definite small partial pressure and with the solid chloropalladate. Chlorine diluted with nitrogen was passed through the palladium solution and then through a second solution identical with the first, except that it contained no palladium. The concentration of the chlorine dissolved in this second solution was found by iodimetric titration. The sum of the concentrations of the free chlorine and of the combined oxidizing chlorine (corresponding to the quadrivalent and to any trivalent palladium) in the solution was measured by titrating it with hydrazine sulfate and determining the end-point electrometrically. A comparison of this observed concentration of oxidizing chlorine with the concentration of quadrivalent palladium as calculated from the results of the previous determinations of the solubility of potassium chloropalladate showed that there is little, if any, trivalent palladium in the solutions here investigated.

Finally, more precise measurements of the equilibrium of the oxidation reaction were made with normal hydrochloric acid solutions containing known quantities of palladium chloride, but no potassium chloride, the concentrations of free and of combined chlorine being determined in the same way as before. In order to determine the effect of hydrogen ion and of chloride ion on the equilibrium, some measurements were made also in 0.3 N hydrochloric acid solutions and in solutions 0.7 N in sodium chloride and **0.3** N in hydrochloric acid.

This research was suggested by Professor A. A. Noyes, and to him and to Dr. Don M. Yost the author is indebted for many helpful suggestions made during the investigation.

Preparation of the Substances and Solutions

The stock solutions of palladous chloride used in these experiments were prepared from pure palladium foil. This was dissolved in aqua regia, and the nitric acid was then destroyed by repeated evaporations with hydrochloric acid. The residue of palladous chloride was heated to 300° until all of the free acid was driven off, and the solution was made up by dissolving this salt in a standard 1 *N* hydrochloric acid solution and filtering to remove any metal formed by decomposition. The palladium content of the stock solution was determined by gravimetric analyses.

The palladium metal was carefully purified before preparing the palladium chloride solution which was used in the final experiments on the equilibrium of the oxidation reaction. About 2.5 *g.* of the foil was converted to palladous chloride as before, and the slightly acid solution of this salt was treated with an excess of mercuric cyanide, whereby the palladium was precipitated as the flocculent, cream-colored cyanide, $Pd(CN)_2$. This was allowed to settle for a few hours, and was then washed several times by decantation; it was not freed from mercury owing to the difficulty of filtering the precipitate.

Ignition of the precipitate first in oxygen then in hydrogen at 800° volatilized the mercury, leaving the palladium as metal. This was again converted to the chloride, and by treating the solution with ammonium hydroxide and hydrochloric acid the palladium was twice precipitated as palladosammine chloride, $Pd(NH_3)_2Cl_2$, which was washed with dilute hydrochloric acid. The chloride solution obtained by boiling this precipitate in acid was saturated with potassium chloride and chlorine; and the potassium chloropalladate was filtered off and ignited in hydrogen. From the pure palladium metal so obtained the stock solution was prepared and standardized as previously described.

All of the dilute thiosulfate solutions required for the iodine titrations were made up as needed from a stock solution of 0.1 N sodium thiosulfate. This was prepared from freshly boiled distilled water and a high grade of thiosulfate, and to each liter of the solution 0.2 *g.* of sodium carbonate was added as recommended by Kolthoff[2] to prevent decomposition. This solution was standardized against standard solutions of potassium permanganate and of potassium dichromate according to the methods described by Bray and Miller.[3] In four months the stock solution so prepared had changed in concentration less than 0.1%. It was also found that the ten-fold or hundred-fold diluted solutions, if used within an hour of the time of their preparation, had the corresponding strength within 0.1%.

The solution of hypochlorous acid used in the electrometric titrations was prepared by passing chlorine gas into a suspension of mercuric oxide in water, and by twice distilling the solution over mercuric oxide to free it from chloride ion. By diluting the distillate, a solution 0.01 N in HClO was thus obtained.

The hydrazine sulfate solution was prepared from the recrystallized salt, and was diluted to approximately the same strength as the hypochlorous acid.

Methods of Analysis

Determination of Total Palladium.—The total palladium present in the solutions was determined by precipitating it as the palladous salt of dimethylglyoxime.[4] The palladium precipitate is too soluble to be washed with hot water, since 1 mg. dissolves in 200-300 cc. of boiling water; but when 0 25 g. of palladium was precipitated from a liter of cold 0.5 N hydrochloric acid, only 0.3 mg. was found in the filtrate. It was found that the compound is not hygroscopic, can be dried to constant weight at 110°, and does not decompose at 130". In this work the palladium was, therefore, determined by weighing the dry dimethylglyoxime precipitate. The palladium determined by evaporating portions of the stock solution in weighed porcelain boats and igniting the residue in hydrogen checked within 0.5% with that calculated from corresponding analyses by this dimethylglyoxime method, although only 50 mg. of palladium was used for each analysis. The dimethylglyoxime method has the additional advantage that the compound contains only a fairly small proportion (31.68%) of palladium. The flocculent light yellow precipitate, which has a composition like that of the familiar nickel compound, is not difficult to filter through perforated crucibles (unless there is more than 0.25 g. of it).

The procedure adopted for the palladium analysis was as follows. Add a solution of about 0.2 g. of dimethylglyoxime in 100 cc. of boiling water to the palladium solution

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[2] Kolthoff, C. *A.*, 13, 3103² (1919).

[3] W. C. Bray and Miller, THIS JOURNAL, 46,2204 (1924).

[4] Wunder and Thiiringer, *Z.* anal. Chem., 52, 101–104, 660-664 (1913); Davis, *C. A.*, 16, 2280⁴ (1922); Cooper, C. *A.*, 20, 10426 (1925). These investigators all converted the precipitate by ignition to metallic palladium.

diluted to 200–300 cc., boil the mixture and allow it to stand overnight; then filter it through a weighed crucible and wash the precipitate with cold water until free from chloride ion; dry it at 110° for an hour and weigh. Subsequent weighinga agreed nearly always within 0.2 mg. and separate analyses usually agreed also within 0.2 mg.

Determination of the Free Chlorine.—The chlorine dissolved in the acid solution through which the diluted gas was passed in the equilibrium experiments was determined by adding potassium iodide and titrating the liberated iodine with 0.001-0.005 N thiosulfate using starch as indicator. A known volume of the solution was run from the apparatus into 600 cc. of distilled water containing 2 g. of potassium iodide. A blank titration was always made and the correction applied, but the indistinctness of the end point caused considerable difficulty, especially when 0.001 N thiosulfate was used for the titration.

Determination of the Total Oxidizing Chlorine.—To determine the combined oxidizing chlorine and the free chlorine dissolved in the palladium solutions, only the electrometric titration could be employed. A known volume of chlorinated palladium chloride solution was run out of the apparatus into a mixture of 200 cc. of water containing 2 g. of potassium bromide with such a volume of the standard 0.01 N hydrazine sulfate solution that there was little or no excess of bromine liberated (not more than 0.03 milliequivalent). A platinum plate was placed in the solution; this was connected with a calomel electrode (with 0.5 N potassium chloride), and the end-point was determined with the aid of an ordinary potentiometer when more hydrazine sulfate was added or the solution was titrated back with hypochlorous acid. The end-point was determined several times with the same solution in order to standardize the hypochlorous acid at the same time. Until the end-point was reached, the potential remained a little above 0.7 volt; but a single drop of 0.01 N hydrazine solution would then reduce this potential by 0.06 volt, while any further addition caused a far more gradual change in potential. In some cases the same palladium solution was after this titration used for determining the total palladium by a dimethylglyoxime precipitation.

Standardization of the Hypochlorous Acid.—The hypochlorous acid solution was standardized by adding potassium iodide and titrating with 0.01 *N* thiosulfate solution. It was then at once used in the subsequent electrometric titrations.

Standardization of the Hydrazine Solution.—Bray and Cuy[5] have shown that the reaction of hydrazine sulfate with bromine is quantitative in acid or neutral solution but that with hypochlorous acid one must add phosphate to buffer the solution and thus prevent loss of chlorine. It was found, however, that by adding potassium bromide to the hydrazine sulfate solution before running in the hypochlorous acid the loss of chlorine or bromine was avoided, for the results by this method of standardization checked with those obtained by the method of Bray and Cuy with bromine solution. Moreover, it was found that palladium salts do not interfere: the quadrivalent palladium is readily reduced to the bivalent state by the hydrazine sulfate, but there is no further reduction at room temperature in the presence of the bromide and some acid.

The procedure adopted for the standardization of the hydrazine was therefore as follows: 25 cc. of the solution was pipetted into 100 cc. of a 0.01 N hydrochloric acid solution containing 1 g. of potassium bromide. Then into this solution was pipetted 25 cc. of freshly standardized hypochlorous acid solution which was a little stronger than the hydrazine solution. The vessel was stoppered, and after five minutes 1 g. of potassium iodide was added, and the iodine liberated by the excess of bromine was titrated with 0.01 *N* thiosulfate solution. To check the results obtained by this method, the excess of bromine in some cases was titrated electrometrically with hydrazine sulfate, whereby the same results were obtained.

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[5] W. C. Bray and Cuy, THIS JOURNAL, 46,858–875 (1924)

Apparatus and Procedure

The Solubility Experiments,—A water thermostat regulated to 25.00 ± 0.02° was used for all the experiments. The solubility apparatus consisted, as shown in Fig. 1, of a glass-stoppered 100-cc. round-bottomed flask having a tube fused into the bottom and a side-tube fused into the neck The chlorine gas was passed from an iron cylinder first through 1 *N* hydrochloric acid in the thermostat, then through four such flasks in series, so that four separate experiments were carried on simultaneously. The chlorine entered the flask at I and escaped from it at O. As connectors were used rubber tubes which had been previously soaked in hot paraffin to prevent their being acted upon by the gas Samples were removed from time to time for the palladium analysis.

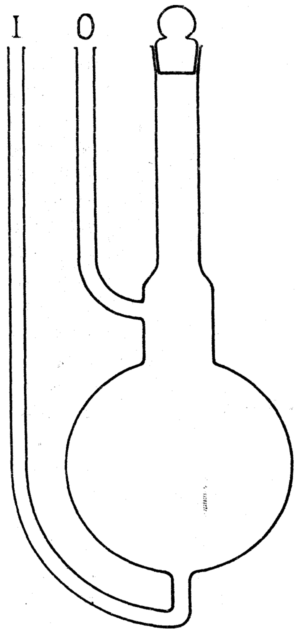

Fig. 1.

The solutions were made up by pipetting into each flask various volumes of the stock solutions of palladous chloride, potassium chloride and hydrochloric acid, and by adding also about 0.25 g. of finely powdered potassium chloropalladate.

To withdraw a sample the stopper was removed and the liquid was drawn quickly from the flask into a partially evacuated vessel through a glass tube containing a plug of asbestos fibers held in place by glass wool and by constrictions in the tube. In this way the solution remained saturated with chlorine until it had passed through the filter. Of this filtered solution 25 cc. was pipetted into a beaker, the chlorine boiled off, and the palladium precipitated with dimethylglyoxime and weighed. Fresh samples were often withdrawn from the flask several days later, in order to show whether the solution had come to equilibrium with the solid phase.

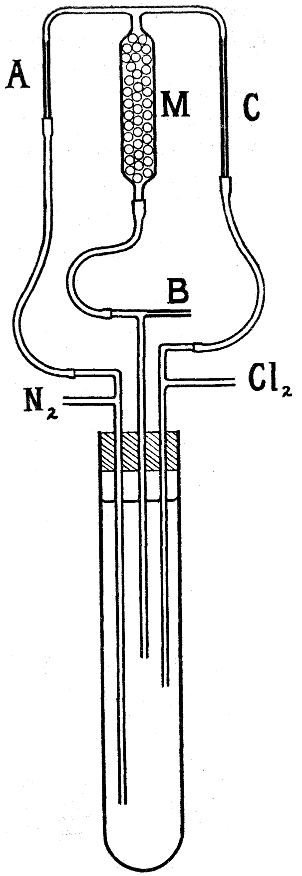

Fig. 2.

Preparation of **the** Chlorine–Nitrogen Mixture.—In all the measurements of the equilibrium of the oxidation reaction it was necessary to dilute with nitrogen the chlorine bubbled through the equilibrium mixtures, since otherwise the palladium would have been completely oxidized. The apparatus shown in Fig. 2 served to produce the gas mixture and to keep it at constant composition within 1–27, during an entire experiment, which lasted in some cases as long as five days. Chlorine from the cylinder entered one arm of a T-tube, the stem of which dipped about half a meter below the surface of concentrated sulfuric acid in a tall glass cylinder 5 cm. in diameter. The other arm of the T-tube was connected through a very fine capillary tube C (which served as a resistance to the flow of chlorine) with the mixing chamber M, consisting of a 50-cc. glass tube filled with beads. In a similar way nitrogen was led from the tank into the mixing chamber. The mixed gases leaving the chamber then entered one arm of a third T-tube whose stem dipped below the surface of the acid only far enough to give the pressure needed to drive the gases through the third capillary B into the equilibrium vessel at the desired rate. The partial pressure of chlorine was thus controlled by duly selecting the three capillaries, A, B, C, and by raising or lowering the tubes dipping into the sulfuric acid.

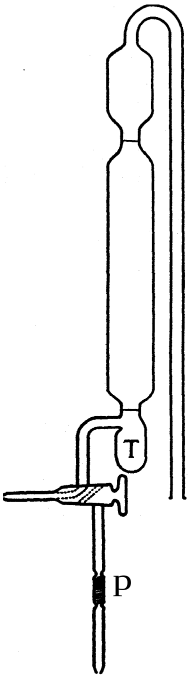

Fig. 3.

Measurement of the Reaction Equilibrium.—The first equilibrium measurements were made in the presence of solid potassium chloropalladate. The equilibrium mixtures were made up in just the same way as for the simple solubility determinations. The apparatus consisted of two calibrated 50-cc. pipets. The diluted chlorine was passed first through the palladous chloride solution in the one pipet, and next through a solution in the second pipet which contained acid and potassium chloride at the same concentrations, but no palladium. The first of these pipets, shown in Fig. 3, was provided with a trap T to catch most of the solid salt, and with an exit tube containing a plug, P, of asbestos fibers to retain the finer particles. The gas was allowed to flow for several days through the apparatus kept in the thermostat. The pipets were then removed from the thermostat one at a time and were inverted while leaving the gas line attached, so that the measured volume of solution could be drawn off without changing the chlorine concentration. These samples were titrated as described above. Since some of the palladium crystallized out as potassium chloropalladate, a gravimetric analysis for palladium had to be made. For this purpose the solution was used in which the chlorine content had already been determined by the electrometric titration with hydrazine.

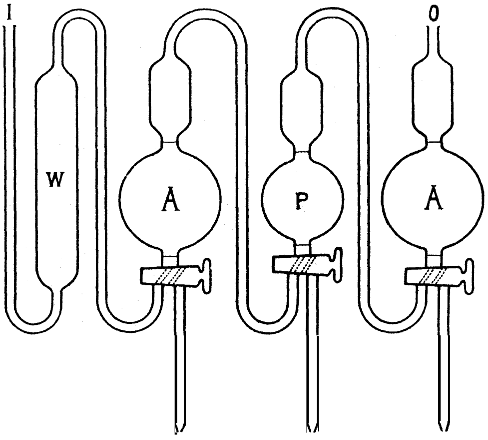

Fig. 4.

For the final experiments in which no potassium chloride was added and no solid potassium chloropalladate separated, an all-glass apparatus was designed as shown in Fig. 4. The vessel W contained hydrochloric acid of the strength prevailing in the reaction mixture. The small 50-cc. bulb P in the middle contained the solution of palladous chloride in hydrochloric acid, and the two 100-cc. bulbs AA at the sides contained a solution of the pure acid of the same concentration. The diluted chlorine was passed through the apparatus in the thermostat for three hours only, for experiments in which the equilibrium was approached from the other side by passing at first pure chlorine and then the diluted gas, showed that equilibrium is reached within two hours with this apparatus. To remove the samples for titration, the chlorine tube was attached to the other end O of the apparatus, so that the same partial pressure of chlorine was maintained above each surface while the solutions were drawn off. The two pure acid solutions were titrated for the dissolved chlorine, and the average value was taken.

The Solubility of Potassium Chloropalladate

The results of the solubility measurements are given in Table I. The solution always was 1.0 N in hydrochloric acid and saturated with chlorine at the atmospheric pressure (about 740 mm.) at 25°.

TABLE I

SOLUBILITY OF POTASSIUM CHLOROPALLADATE AT 25° IN NORMAL HYDROCHLORIC ACID SATURATED WITH CHLORINE AND CONTAINING POTASSIUM CHLORIDE

Expt. no.	Time, days	Saturation[a]	Pd ppt. in mg., found	Pd ppt. in mg., mean	Palladium Initial	Palladium Final	Potassium Initial	Potassium Final	Solv. prod. × 10^6
1	1	u	125.0	125.2	18.28	14.86	26.92	20.08	5.99
	5	s	125.3						
	8	s	125.4						
2	8	s	95.2	95.2	13.28	11.30	26.92	22.96	5.96
	11	s	95.3						
3	1	u	50.6	50.7	8.80	6.02	37.04	31.48	5.97
	3	u	50.7						
	5	s	50.7						
	8	s	50.9						
4	8	s	42.1	42.2	6.39	5.01	37.04	34.28	5.89
	11	s	42.4						
5	1	u	37.6	37.4	9.14	4 44	46.15	36.75	6.00
	3	u	37.5						
	5	s	37.2						
	8	s	37.2						
6	8	s	27.0	27.0	4.00	3.21	44.44	42.86	5.90
	11	s	27.0						
7	1	u	16.7	16.8	3.32	1.99	57.69	55.03	6.04
	3	u	17.0						
	5	s	16.7						
	8	s	17.0						
8	8	s	13.2	13.2	3.32	1.57	65.39	61 89	6.00
	11	s	13.2						
								Mean value	5.97

[a] The letter u denotes previous undersaturation with K_2PdCl_6, which was attained by freezing it out at the start of the experiment. The letter s denotes previous supersaturation with K_2PdCl_6, attained by keeping the solution at 25° from the start or by warming it to 40° at the beginning.

The initial concentrations of palladium and potassium were known from the proportions of the stock solutions used in preparing the mixtures. The final palladium concentration was calculated from the weight given in the column headed "Pd ppt. in mg.," which shows the number of milligrams of the glyoxime compound obtained from 25.0 cc. of the saturated solution. Since some chloropalladate always crystallized out before equilibrium was attained, the final potassium concentration was found by directly determining the decrease in the palladium content and correcting the initial potassium content accordingly. All these concentrations are given in the table in millimoles per liter. The values of the solubility product, $(K^+)^2\ (PdCl_6^{--})$, were calculated from the final molal concentrations of potassium and palladium. In this calculation all of the palladium was considered to be in the quadrivalent state in the form of the complex ion, $PdCl_6^{--}$, for the determinations of the equilibrium constant described below show that less than 0.5% is in the palladous state in a solution saturated with chlorine at atmospheric pressure.

It will be seen that, though the potassium concentration was altered three-fold and the palladium concentration thereby varied nine-fold, yet the solubility product remained nearly constant. The mean value of the solubility product at 25° is 5.97×10^{-6}. This value, it should be noted, is that prevailing when the solvent is 1 N hydrochloric acid saturated with chlorine at 740-mm. pressure.[6]

Equilibrium of the Oxidation Reaction in the Presence of Solid Potassium Chloropalladate

The results of the experiments are presented in Table II. All of the concentrations are given in millimoles per liter, but in evaluating the equilibrium constant the concentrations were expressed in moles per liter.

In the first column is given the experiment number, to which is attached a letter u or s showing the direction in which the equilibrium was approached. The letter u indicates that the solution was originally undersaturated with respect to potassium chloropalladate, for this salt was crystallized out at the start by passing undiluted chlorine through the solution in an ice-bath. The letter s denotes that the solution was originally supersaturated with chloropalladate, for the diluted chlorine was passed through the mixture in the thermostat from the start.

The second column shows the number of days during which the dilute chlorine was passed through the solution in the thermostat before taking the samples for analysis.

In the third column are given the concentrations of potassium in the equilibrium solution. These were derived from the initial values and from the decreases in palladium content determined as in the solubility experiments.

In the fourth column, headed "free chlorine," is given the concentration of free (uncombined) chlorine dissolved in the equilibrium solution. The value given is the concentration of chlorine in the acid solution increased by 2.2%, to allow for the difference in the pressure of gas in the

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[6] The value corresponds to a solubility of 0.0114 molal, which is somewhat less than the solubility (0.0179 m.) of potassium chloroplatinate in water at 25° [Archibald, Wilcox and Buckley, THIS JOURNAL, **30,** 752 (1908)].

two pipets. The chlorine dissolved in the acid solution was determined by titrating with dilute thiosulfate the iodine liberated from potassium iodide.

In the fifth column, headed "total chlorine," is given the total oxidizing chlorine of the equilibrium solution. This was the value determined by the electrometric titration, for both the free chlorine and the chlorine combined with the quadrivalent palladium (as well as with any trivalent palladium) are reduced by the hydrazine.

In the sixth column, headed "$PdCl_6^{--}$ obs.," is recorded one-half of the value obtained by subtracting from the total chlorine the free chlorine found in the pure acid solution. These values represent the concentration of this ion under the assumption that there is no trivalent palladium in the solution.

In the seventh column, headed "$PdCl_6^{--}$ calcd.," are shown the concentrations of the chloropalladate ion as calculated from the mean value of the solubility product given in Table I. These should be the actual $PdCl_6^{--}$ concentrations provided the solubility equilibrium is attained.

In the eighth column are given the differences between the concentrations in the sixth and seventh columns. Except for experimental error these differences should be half the molal concentration of the $PdCl_5^{--}$ if it also exists in the equilibrium mixture.

In the ninth column, headed "Total Pd," are given the concentrations of palladium obtained by the precipitation of the palladium with dimethylglyoxime after the solutions had been titrated with hydrazine for total chlorine.

In the tenth column under the heading "$PdCl_4^{--}$," are shown the concentrations of bivalent palladium as found from the difference between the palladium content given in the preceding column and the "observed

TABLE II

EQUILIBRIUM DATA FOX THE OXIDATION REACTION IN NORMAL HYDROCHLORIC ACID IN THE: PRESENCE OF SOLID POTASSIUM CHLOROPALLADATE AT 25°

Expt.	Time, days	Potassium	Free chlorine	Total chlorine	Millimoles of $PdCl_6^{--}$			Total Pd	$PdCl_4^{--}$	Equil. const.
					obs.	calcd.	diff.			
1 u	1	494	0.117	266	254	2.45	009	860	6.06	3580
2 u	1	47.1	.167	290	274	2.69	05	7.46	472	3480
3 s	3	46 9	.184	3.10	2 92	2.71	.21	7.35	4.43	3580
4 s	5	46 4	.204	3.15	2.95	2 77	.18	7.11	4.16	3480
5 s	1	45 6	.282	3 61	3.33	2 87	46	6 70	3 37	3500
6 u	1	42 9	.442	3 75	3.31	3 24	07	5.36	2.05	3650
7 u	1	321	1.18	722	604	579	.25	7.47	1.43	3580
8 u	1	31.4	2.00	8 26	6.26	6 06	.20	7.10	0.84	3740
9 u	5	28.3	2 04	9.13	7 59	7.43	.16	8.57	.98	3810
10 u	4	28.9	2.17	9.69	752	715	37	8.41	.89	3900
11 s	1	28.7	2.63	1013	750	7.25	25	826	.76	3750
									Mean	3640

$PdCl_6^{--}$" in the sixth column. The "calculated $PdCl_6^{--}$" could not be used, since in many cases equilibrium with the solid was not attained.

In the last column are given the values for the equilibrium constant calculated by the expression $(PdCl_6^{--})/(PdCl_4^{--})(Cl_2)$, using for the (Cl_2) the concentration of "free chlorine" and for $(PdCl_6^{--})$ the "observed" concentration given in the sixth column.

It will be seen from Table II that in every experiment the $PdCl_6^{--}$ concentration determined by the hydrazine titration is greater than that calculated from the solubility of potassium chloropalladate. This difference is smaller in Expts. 1, 2 and 6, but this may arise from the fact that only one day was allowed for the approach to equilibrium, and that therefore the solutions may have been still undersaturated with chloropalladate. The equilibrium between solution and solid was probably attained in the other experiments, where several days were allowed for the approach to equilibrium. There seems, therefore, always to be between the calculated and observed $PdCl_6^{--}$ concentrations a real difference, usually amounting to about 20 millimoles per liter, which seems greater than can be accounted for by experimental errors. This difference may be due to the presence in the solution of some trivalent palladium.[7] At any rate the experiments prove that the amount of palladium present in the trivalent state is small compared with the amounts in the other two states in these solutions, and the concentration of it was neglected in the calculations of the equilibrium constant of the oxidation reaction.[8]

It will also be seen from Table II that the values of the equilibrium constant show an average deviation from the mean of only 3.2% and that the extreme deviation from the mean is 7.1%.[9]

Equilibrium of the Oxidation Reaction with No Solid Phase Present

The results of the equilibrium experiments where no solid phase was present are given in Table III. All the concentrations are given in millimoles per liter, but the equilibrium constant is again expressed in moles.

The first column gives the experiment number, to which an asterisk

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[7] The fact that the difference is substantially constant throughout the whole series of experiments is also in accord with the assumption that this difference is due to trivalent palladium; for, by the mass action law, $(PdCl_5^{--})/(PdCl_6^{--}) = K/(Cl_2)^{1/2}$, and it happens that in the experiments $(PdCl_6^{--})$ was approximately proportional to $(Cl_2)^{1/2}$.

[8] It might seem better, in view of the possible presence of trivalent palladium, to use for $(PdCl_6^{--})$ the values calculated from the solubility of the K_2PdCl_6; but the solubility equilibrium, unlike the equilibrium of the oxidation reaction, is established so slowly that saturation with the solid phase was not always reached.

[9] The agreement between the individual results is of the order one would expect. For an error of 0.5 mg. in the gravimetric analysis for total palladium, in Expts. 1 and 11 for example, would make errors in the constant of 0.5 and 3.0%, respectively, and an error of 0.2% in the electrometric titration would produce errors in the constant of **0.3** and 2.0%, respectively.

is attached when the experiment was made with the first palladium preparation, not with the final carefully purified one.

The second column shows the mean concentration of free chlorine as found from the titrations of the two pure acid solutions.

In the third column is given the concentration of total oxidizing chlorine found by the titration of the equilibrium mixture with hydrazine.

The fourth column, headed "$PdCl_6^{--}$," shows the concentration of quadrivalent palladium, under the assumption that this is equal to one-half of the difference between the total and free chlorine.

TABLE III

EQUILIBRIUM DATA FOR THE OXIDATION REACTION AT 25° WITH NO SOLID PHASE

A. Experiments with solutions 1 N in hydrochloric acid

Expt.	Free chlorine	Total chlorine	$PdCl_6^{--}$	Total Pd	$PdCl_4^{--}$	Equil. const.	Per cent. deviation
1	0.109	1.58	1.47	5.11	3.64	3700	−0.3
2*	.131	3.29	3.16	9.40	6.24	3780	+1.8
3*	.136	3.33	3.19	9.40	6.21	3780	+1.8
4	.160	2.01	1.85	5.11	3.26	3550	−4.3
5	.160	2.04	1.88	5.11	3.23	3640	−1.8
6	.159	3.86	3.70	10.22	6.52	3570	−3.8
7	.225	2.58	2.36	5.11	2.75	3810	+2.7
8	.230	2.55	2.32	5.11	2.79	3620	−2.4
9*	.496	6.68	6.18	9.40	3.22	3870	+4.3
10	.537	7.27	6.73	10.22	3.49	3670	−1.1
11	.538	7.34	6.80	10.22	3.42	3700	−0.3
12	.564	4.02	3.46	5.11	1.65	3720	+0.3
13*	.586	7.07	6.48	9.40	2.92	3790	+2.2
14	.592	4.08	3.49	5.11	1.62	3720	+0.3
15	.994	5.03	4.04	5.11	1.07	3800	+2.4
16	1.00	5.02	4.02	5.11	1.09	3690	−0.5
17	1.22	5.40	4.18	5.11	0.93	3680	−0.8
18	1.23	5.43	4.20	5.11	0.91	3750	+1.1
						Mean 3710	±1.8

B. Experiments with solutions 0.3 N in hydrochloric acid and 0.7 N in sodium chloride

Expt.	Free chlorine	Total chlorine	$PdCl_6^{--}$	Total Pd	$PdCl_4^{--}$	Equil. const.	Per cent. deviation
19	0.211	2.41	2.20	5.11	2.91	3580	−3.5
20	.224	2.50	2.28	5.11	2.83	3600	−3.0
21	.712	4.45	3.74	5.11	1.37	3830	+3.2
22	.737	4.51	3.77	5.11	1.34	3820	+3.0
						Mean 3710	±3.2

C. Experiments with solutions 0.3 N in hydrochloric acid

Expt.	Free chlorine	Total chlorine	$PdCl_6^{--}$	Total Pd	$PdCl_4^{--}$	Equil. const.	Per cent. deviation
23	0.164	2.08	1.92	5.11	3.19	3670	+2.2
24	.173	2.13	1.96	5.11	3.15	3600	+0.3
25	.494	3.74	3.25	5.11	1.86	3510	−1.4
26	.497	3.76	3.26	5.11	1.85	3550	−1.1
27	.938	4.89	3.95	5.11	1.16	3630	+1.1
28	.956	4.91	3.95	6.11	1.16	3560	−0.8
						Mean 3590	±1.2

In the fifth column, under the heading "Total Pd," is given the total palladium content, calculated from the volume of the standard stock solution used in preparing the equilibrium mixture.

In the sixth column, under the heading "$PdCl_4^{--}$," is given the concentration of bivalent palladium found by subtracting the "$PdCl_6^{--}$" from the "Total Pd."

In the seventh column are given the equilibrium constants for the reaction as calculated from the molal concentrations of free chlorine, $PdCl_6^{--}$, and $PdCl_4^{--}$. In the last column are shown the percentage deviations of these values from the mean value.

Discussion of the Equilibrium Data

It will be seen from the experiments in Series A of Table III that, though the concentration of free chlorine was varied more than ten-fold and the concentration of palladium was doubled, yet the equilibrium constants show a maximum deviation from the mean of only 4.3%, and an average deviation from the mean of only 1.8%. Moreover the mean value, 3710, of the constant differs only by 1.9% from the mean value, 3640, obtained in the experiments recorded in Table II. We shall adopt 3710 for the equilibrium constant in normal hydrochloric acid solution, since the average deviation (1.8%) was considerably less than that (3.2%) in the experiments of Table II.

The fact that the experimentally determined equilibrium constant does not vary with the concentration of free chlorine shows that little, if any, trivalent palladium is present in the solution; for its concentration would, in accordance with the mass action expression $(PdCl_5^{--})/(PdCl_4^{--}) = K'(Cl_2)^{1/2}$, be proportional to the square root of the chlorine concentration.

In the preceding considerations it has been assumed that the "free chlorine" is all present as chlorine molecules. It is, however, known that dissolved chlorine exists also in the form of hypochlorous acid and of trichloride ion. So long as the hydrogen-ion and chloride-ion concentrations in the solution are constant, as in the experiments of any one series, the various proportions of these three forms of chlorine will be constant, as is seen from the following expressions for the equilibria involved

$$K_H = \frac{(H^+)\ (Cl^-)\ (HClO)}{(Cl_2)} \qquad K_C = \frac{(Cl_3^-)}{(Cl_2)\ (Cl^-)}$$

Change of the chlorine concentration should therefore not cause variation of the calculated equilibrium constants of the reaction within any one series, where the hydrogen-ion and chloride-ion concentrations were kept the same. Nevertheless, a divergence of the value of the concentration of the "free chlorine" from that of Cl_2 as such would affect the numerical value of the constant. Moreover, in the case of the Series

A, B and C, where the concentrations of hydrogen ion and chloride ion differ, such a divergence might cause a difference between the equilibrium constants of these three series. It is therefore necessary to consider the magnitudes of these effects of hydrolysis and complex ion formation.

From the value 4.84×10^{-4} for K_H given by Lewis and Randall[10] and from the activity coefficients of the hydrogen ion and chloride ion given by them (Ref. 10, p. 336) the ratio $(HClO)/(Cl_2)$ can be calculated. The calculation shows that in 1 N hydrochloric acid the hydrolysis of chlorine is entirely negligible (less than 0.1%), and that even in 0.3 *N* hydrochloric acid it amounts to only 0.9%, while in a solution 0.7 N in sodium chloride and 0.3 *N* in hydrochloric acid it is about 0.3%.

The ratio of the concentration of Cl_3^- to total Cl_2 in these solutions may be found from the results obtained by Sherrill and Izard[11] on the solubility of chlorine in solutions of hydrochloric acid and of sodium chloride. This ratio was found by them to be 0.154 in 1 N hydrochloric acid, and by interpolation it is found to be 0.049 in 0.3 *N* hydrochloric acid, and 0.150 in a solution 0.3 N in hydrochloric acid and 0.7 N in sodium chloride.

Moreover, the assumptions were made in calculating the equilibrium constants given above that the ratio of the concentrations of $PdCl_6^{--}$ and $PdCl_4^{--}$ was equal to the ratio of their activities, and that the concentration of Cl_2 was equal to its activity. The first of these assumptions is probably essentially correct, in view of the similarity of the two ions, but the activity coefficient of the chlorine is known to vary with change in the concentrations of hydrogen ion and chloride ion. Its activity coefficient is given by the ratio of the solubility of chlorine as such (Cl_2) in pure water to the solubility of chlorine in the equilibrium mixture. This is shown by the calculations of Sherrill and Izard to be 1.053 in 1 N hydrochloric acid and by interpolation is found to be 1.015 in 0.3 N hydrochloric acid and 1.238 in 0.7 N sodium chloride. Its activity coefficient in a solution 0.7 N in sodium chloride and 0.3 *N* in hydrochloric acid is 1.258 under the assumption that the salting-out effects of the hydrochloric acid and sodium chloride are additive.

In accordance with these considerations the concentration of chlorine as such (Cl_2) was determined by subtracting from the concentration of the "free chlorine" the concentrations of HClO and of Cl_3^- calculated from the ratios above; then its activity was found by multiplying the resulting concentration of Cl_2 by the activity coefficient for chlorine in the equilibrium mixture. By using this activity of chlorine as such in place of the concentration of free chlorine, the values calculated from the three

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[10] Lewis and Randall, "Thermodynamics," p. 508, calculated this value from the work of Jakowkin.

[11] Sherrill and Izard, private communication concerning a research at the Massachusetts Institute of Technology, 1929.

mean values given in Table III for the equilibrium constant of the oxidation reaction are found to be 4160 in 1 *N* hydrochloric acid, 3480 in a solution 0.7 N in sodium chloride and 0.3 N in hydrochloric acid, and 3750 in 0.3 N hydrochloric acid.

It will be seen that a 3.3-fold decrease of the concentration of the hydrogen ion, while that of the chloride ion is kept constant, does not have a large effect on the equilibrium constant. This indicates that little of the palladium in these solutions is in the form of hydrolyzed acids, such as $H_2PdCl_2(OH)_2$ or $H_2PdCl_5(OH)$, or in the state of un-ionized acids.

It will also be seen that a 3.3-fold decrease in the concentration of the chloride ion, while that of the hydrogen ion is kept constant, causes only a small change in the mean value of the equilibrium constant. This fact proves that the bivalent palladium and the quadrivalent palladium must both be nearly or quite completely in the form of such complex ions as result from the addition of the same number of chloride ions to the simple chlorides ($PdCl_2$ and $PdCl_4$); for otherwise the chloride-ion concentration would appear in the equilibrium expression and would greatly affect the value of the constant calculated as above without taking this into account. In view of the solid salts known to be formed from quadrivalent palladium in chloride solution and of its analogy with quadrivalent platinum, there is therefore little doubt that the two complex ions present are almost wholly $PdCl_6^{--}$ and $PdCl_4^{--}$.

The Reduction Potential of Bivalent–Quadrivalent Palladium in Chloride Solutions

The free-energy decrease $-\Delta F$ attending the reaction $PdCl_4^{-} + Cl_2 = PdCl_6^{--}$ when all the substances have an activity of 1.0 molal, is found by the formula $-\Delta F = RT \ln K$ to be 20,620 joules, using for the equilibrium constant K the corrected value 4160 in 1.0 N hydrochloric acid. The corresponding potential E obtained from the expression $E = -\Delta F/2 \times 96{,}500$ is 0.1070 volt. For the case that the chlorine has a partial pressure of one atmosphere the potential for the reaction is 0.0707 volt. This is found by correcting the potential by $^1/_2(RT/F) \ln c$ (or 0.0296 log c), where c represents the solubility (0.0592 molal) in water of chlorine gas when its partial pressure is one atmosphere.

The equation for the free energy is therefore

$$PdCl_4^{--}\ (1\ \text{m.}) + Cl_2\ (1\ \text{atm.}) = PdCl_6^{--}\ (1\ \text{m.}) + 2F \times 0.0707\ \text{joule}$$

The following equation expresses the reduction potential of Cl_2 (1 atm.) Cl^- (1 m.), when E^- represents one mole of electrons

$$2Cl^-\ (1\ \text{m.}) = Cl_2\ (1\ \text{atm.}) + 2E^- - 2F \times 1.359\ \text{joules}$$

Adding these two equations, one obtains, when all three ions are 1.0 molal

$$PdCl_4^{--} + 2Cl^- = PdCl_6^{--} + 2E^- - 2F \times 1.288\ \text{joules}$$

The reduction potential of $PdCl_4^{--} + 2Cl^-$ (reduced state) with respect to $PdCl_6^{--}$ (oxidized state) is therefore **-1.288** volts at 25°.

Summary

Measurements have been made of the solubility at 25° of potassium chloropalladate (K_2PdCl_6) in normal hydrochloric acid containing potassium chloride and saturated with chlorine at atmospheric pressure, and the value 5.97×10^{-6} has thus been found for the solubility product $(K^+)^2(PdCl_6^{--})$ in moles per liter.

The equilibrium of the oxidation reaction $PdCl_4^{--} + Cl_2 = PdCl_6^{--}$ has been studied. This was first done by using normal hydrochloric acid solutions of palladium chloride saturated both with solid potassium chloropalladate and with chlorine hundred-fold diluted with nitrogen. A comparison of the $PdCl_6^{--}$ concentration calculated from the solubility product for K_2PdCl_6 with that derived from the analytically determined concentration of combined oxidizing chlorine showed that little, if any, trivalent palladium exists in the equilibrium mixture.

More exact measurements were also made of the equilibrium of the oxidation reaction without any solid phase present. The value 4160 was thus found for the equilibrium constant $K = (PdCl_6^{--})/(PdCl_4^{--})/(Cl_2)$ in 1 N hydrochloric acid solution, using in the expression the molal concentrations of bivalent and quadrivalent palladium and the activity of chlorine as such, obtained by subtracting from the total free chlorine the calculated concentrations of HClO and Cl_3^- present and by changing the resulting concentrations of Cl_2 over to activities with the aid of the relative solubilities of chlorine gas in water and in hydrochloric acid.

Values were also found for the equilibrium constant in 0.3 N hydrochloric acid solution, and in a solution 0.3 *N* in hydrochloric acid and 0.7 N in sodium chloride. These values, corrected as just described, were 3730 and 3480, respectively. This shows that these variations in the chloride-ion and hydrogen-ion concentrations do not have a large effect on the equilibrium, and therefore proves that the two complex ions present are those formed from the simple chlorides, $PdCl_2$ and $PdCl_4$, by the addition of the same number of chloride ions, and that they are therefore doubtless $PdCl_4^{--}$ and $PdCl_6^{--}$; also that little of the palladium is in the form of hydrolyzed acids, such as $H_2Pd(OH)_2Cl_2$ or $H_2Pd(OH)Cl_5$.

From the equilibrium constant (4160) in normal hydrochloric acid, the reduction potential for the reaction $PdCl_4^{--} + 2Cl^- = PdCl_6^{--} + 2E^-$ at 25° is computed to be **-1.288** volts.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY]

THE ELECTROMOTIVE BEHAVIOR OF SINGLE ZINC CRYSTALS. THE EQUILIBRIUM POTENTIAL

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An examination of the electromotive characteristics of single metal crystals may be expected to contribute information touching four important problems. (1) It is the present practice in measuring the electrode potentials of the semi-rigid lattice metals, *e.* g., zinc, cadmium and copper, to employ as a standard electrode a finely divided conglomerate of crystals prepared by rapid electrolysis under specified conditions and to assume that the potential of such an electrode, if reproducible, is uniquely characteristic of the element. The study of single crystal electrodes, if such electrodes be found capable of yielding constant and reproducible potentials, offers a means of more clearly defining the significance of measurements on crystal matrices and of studying the more generally important relation between surface structure and potential by connecting an observed potential with a structure definitely describable in the crystallographic sense. (2) It has heretofore been found impossible to prepare satisfactorily reproducible electrodes of the rigid lattice metals, *e.* g., iron and nickel; the marked discrepancies in the measurements reported by various observers may be attributed, at least in part, to differences in physical structure conditioned by the arbitrary methods of preparation adopted and to unknown quantities of gas held in solution in the interstitial layers of the polycrystalline metal, difficulties which should be minimized by the use of single crystals. **(3)** The establishment of a reproducible potential for a single strain-free crystal would seem to furnish the only sound basis for the study of the relation between mechanical strain and electrode potential. (4) The coordination of electromotive and photoelectric data which is possible at present only for the soft alkali metals requires that both measurements be made upon comparable specimens of the metal. A finely divided matrix is not well adapted to photoelectric or contact potential measurement while the massive specimens generally employed in photoelectric determinations do not give reproducible potentials in electrolytes. It is an open question whether any two polycrystalline mosaics are strictly comparable and the influence of crystal orientation has to be considered.[2] It seems probable that the correlation of the electromotive, photoelectric, and vapor pressure characteristics of single metal crystals will throw light on the mechanism of the reaction

$$\text{M (atom in surface lattice)} \longrightarrow \text{M}^{n+} \text{ (in solution)} + nE \text{ (lattice)}$$

as well as on the various energy transitions involved in this reaction.

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[1] National Research Fellow.

[2] Linder, *Phys. Rev.*, 30, 649 (1927), has obtained evidence for a 2:1 variation in the photoelectric work function between the basal and prismatic orientations of zinc.

The present paper reports measurements designed to appraise the electromotive behavior of a typical, easily prepared crystal, that of zinc, with especial reference to the constancy and reproducibility of the potential of the primary cleavage (0001) face. Some hundreds of measurements on air-free cells of the type

$$Zn, ZnCl_2 \text{ (aq.)}, HgCl, Hg$$

made on fifteen crystals prepared by three different methods have shown conclusively that a single zinc crystal is a reversible electrode capable of yielding potentials constant to a few hundredths of a millivolt arid reproducible over dissimilarly prepared crystals to one or two-tenths of a millivolt.

Experimental

Materials and Equipment.—The zinc employed in the preparation of the electrolyte and matrix electrodes was Kahlbaum's analytical grade purified by two fractional distillations in vacuum and a final electrolytic precipitation. Analytical grade hydrochloric acid was redistilled twice. Water from the laboratory still was redistilled from alkaline permanganate and sulfuric acid. Mercury of good initial purity was washed in the usual tower, redistilled twice in an oxidizing atmosphere, and filtered through a small capillary. Calomel was prepared electrolytically from the purified mercury and hydrochloric acid, washed and dried in vacuum. A small quantity of the purified mercury was redistilled once again, partially converted to calomel, and used in one of two duplicate calomel electrodes in the first cell set up, checking the purity of the main stock. Tank nitrogen was freed from reactive gases by repeated passage over hot potassium in a reciprocating gasometer.

The potentiometer and constant temperature installation were similar to those described in a previous paper[3] except that thermostatic regulation was effected without relays with a Thyratron grid-controlled mercury arc tube. Duplicate Weston cells, thermostated to 25.0° and frequently checked for consistency during the measurements, were calibrated against Bureau of Standards certificated cells immediately before the final measurements.

Preparation of Electrolyte.—Air-free zinc chloride electrolyte was prepared by treating an excess of purified finely divided zinc with purified hydrochloric acid in an all-glass storage flask, diluting with distilled water, boiling, evacuating quickly after closing the flask, and finally passing purified nitrogen during cooling. The storage flask was fitted with side stopcock and siphon delivery tube passing through a ground stopper. The delivery tube carried a glass wool filter, stopcock and junction ground to fit the cell described below. Some difficulty was encountered in obtaining an electrolyte which could be accepted as an equilibrium solution; dissolution of the zinc in the acid was extremely slow, requiring, with the assistance of platinum scraps and continuous warming, about four weeks to attain the approximate completion indicated by cessation of a noticeable evolution of hydrogen. On dilution and again on boiling the basic chloride precipitate appeared. The electrolyte was allowed to stand in contact with the mixture of metallic zinc and basic precipitate at the cell temperature for at least two months before introduction into the cell.

Analyses were carried out on the electrolyte taken from the cell after completion of a series of measurements. Quadruplicate samples were taken from a weight buret and analyzed gravimetrically as silver chloride. Analyses checked to within 0.1%.

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[3] Anderson, THIS JOURNAL, 48, 2286 (1926).

Preparation of Matrix Electrodes.—The platinum spiral cathode usually employed in the preparation of finely divided metal electrodes by rapid electrolysis was replaced with a point cathode, a straight stiff platinum wire extending to within a few millimeters of the end of an open 6-mm. glass tube immersed in the electrolyte. The close current regulation necessary to obtain a deposit of the required character with the spiral cathode is unnecessary with the protected point cathode; beautiful trees of silver-white microcrystals are obtained without any current regulation whatever. When the point is first immersed the current remains of the order of a few milliamperes until the deposit passes the orifice of the tube, then increases rapidly to as much as three amperes as the tree grows without apparent alteration in the character of the deposit. The finely divided metal was washed with distilled water, stored under water and dried in a vacuum desiccator immediately before introduction into the cell.

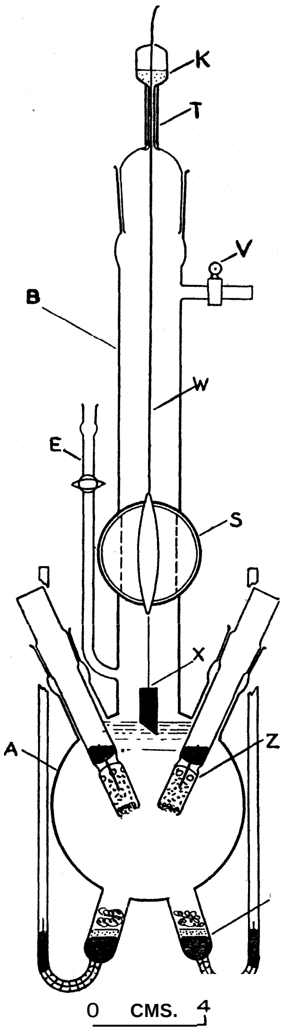

Fig. 1.

The Cell.—It was required that the cell permit of filling with exclusion of air and desirable that it permit of interchanging crystal electrodes without admission of air. The cell proper, A, Fig. 1, carrying duplicate calomel electrodes C and duplicate matrix electrodes Z, is separated from the chamber B by a stopcock of 20-mm. bore. The crystal X is tied to the platinum wire W, which makes a sliding fit in the capillary tube T; the lead wire passes out through sealing wax in the cup K. The matrix electrodes are of a new design allowing a free circulation of electrolyte through the mass of finely divided metal; the metal is packed between glass wool plugs around a stiff platinum wire which extends upward into a mercury cup as indicated.

In filling the cell the crystal was suspended in the vestibule B, the calomel electrodes charged dry through the side tubes, and the matrix electrodes sealed in with an exterior ring of sealing wax. The electrolyte reservoir was connected at E, V connected to vacuum and the nitrogen gasometer. With S and E open, the cell was evacuated up to the stopcock of the electrolyte reservoir, washed out with nitrogen, again evacuated and the required quantity of electrolyte drawn in. The pressure was then brought slightly above that of the atmosphere with nitrogen and the cell disconnected. The crystal electrodes could be lowered or withdrawn without admission of air by warming the sealing wax in K. Interchange of crystals was effected by drawing up the crystal to be discarded, closing S, and replacing the air in the vestibule by nitrogen after introducing the new crystal.

Preparation and Mounting of Crystal Electrodes.—The preparation of an isolated area of a cleavage surface as nearly strain-free and crystallographically perfect as possible is of fundamental importance and a large number of preliminary measurements were made for the purpose of determining the effect of various methods of handling upon potentials. The majority of the crystals measured were monocrystalline rods cast in pyrex tubes by the method of Bridgman.[4] The diameters of these rods varied between 4 and 20 mm.; 6–8 mm. rods were found especially convenient. The rods were removed from the tubing by carefully squeezing the tube in a vise with parallel jaws after cooling with liquid air and fixed in a miter box arrangement with molten sealing wax in such a way as to prevent distortion during cutting. A short section was cut off with a broad bladed jewelers' saw moving in guides and the cleavage located by trial and error on this section. The rod proper was then cooled in liquid air, without direct contact between the metal and liquid air, and split into sections with a sharp knife blade and one-ounce hammer. The liquid air cooling greatly facilitated the cleavage, favored the production of mirror-like planes without visible imperfections, and minimized distortion during cleavage. The crystal sections were heated for at least three hours under paraffin at 200–250° and left in the solidified paraffin until taken out for measurement. Annealing by heating to 400° in vacuum induced recrystallization, which started, apparently, from slightly strained regions. Immediately before introduction into the cell one end of the crystal was tied to the platinum lead wire and a small area in the center of the cleavage face to be measured was cleared of paraffin with a soft wood stylus. The crystal was suspended in the electrolyte in such a way that only this isolated area was exposed. A few crystals prepared by other methods and measured for purposes of comparison are given special consideration in the next section.

Electromotive-Force Measurements.—Table I, which is largely self-explanatory, presents measurements on six crystals made after preliminary work had indicated the approximate experimental conditions required; all measurements on the last six crystals prepared are given without selection of particularly favorable results. The crystals designated as X-1, X-2, X-4, were split Bridgman rods prepared by the method outlined above from zinc of exceptional purity.[5] X-3 was similarly prepared from Kahlbaum's analytical grade zinc without further purification. The crystal X-5, supplied to us by Mr. Cyr and obtained by him incidentally to the purification of zinc by slow distillation, contained an unusually perfect basal plane which had not been subjected to the slightest mechanical deformation. X-6 was a Bridgman rod of the "spectroscopically pure" zinc, with cleavage approximately perpendicular to the rod axis, which was suspended in the electrolyte without isolation of a section of the cleavage face; the electrolyte was in contact not only with the cleavage face but with the sharp edges and sides of the rod. The cells required approximately forty-eight hours to reach equilibrium after filling and readings were made at intervals of from one to eighteen hours thereafter over periods of from four to eight days. The duplicate calomel electrodes checked consistently to 0.01 millivolt. The potentials of four matrix electrodes measured simultaneously with the crystals are given to the nearest tenth millivolt in Table I; these potentials were constant within

[4] Bridgman, *Proc. Am. Acad. Arts Sci.*, *60*, 307 *(1925)*.

[5] Total impurity under 0.0001%. Supplied to us through the kindness of Mr. H. M. Cyr of the Research Laboratory of the New Jersey Zinc Company. Cyr has found that the ordinary properties of this zinc, *e. g.*, resistance to acid attack and behavior under mechanical working, are markedly different from those of ordinarily pure

±0.05 mv. The measurements indicated by asterisks were made two minutes after shaking the cell and show a negligible sensitivity.

TABLE I

OBSERVED POTENTIALS IN VOLTS FOR THE (0001) FACES OF SIX SINGLE ZINC CRYSTALS AT 25°

Electrolyte: 0.4496 *M* $ZnCl_2$(aq.). Elapsed time for each series at least ninety-six hours. Interval between successive readings, one to eighteen hours.

X-1	X-2	X-3	X-4	X-5	X-6
1.07794	1 07786	1 07790	1.07800	1.07801	1,07795
98	83	88	801	800	790
95	82	89	799	802	795
95	85	89	801	803	795
95	82	87	800	802	796
94	84	88*	800	802	796
95	83	88	801	802	797
95*	85*	1.07790	801	802	796
94	84		802	804	799
95	84		801	803*	791
93	84		800	800	790
95	86		801	801	791
97	86		800	800	800
96	85		802	802	1 07797
95	90		1 07801	802	
95	88			802*	
96	90			802	
1.07795	90			801	
	86			802	
	87			1.07803	
	1.07790				

POTENTIALS OF SIMULTANEOUSLY MEASURED MATRIX ELECTRODES

I	II	III	IV
1.0776	1.0778	1.0775	1.0779

From the point of view of the theory of crystal growth and crystal surface energies, the stability of the potential of a crystal face during prolonged contact with the electrolyte and the closely related effect of etching are of importance. In two cases crystals were allowed to stand in contact with the electrolyte for two months; potentials measured at the end of this period checked the original equilibrium potential to within 0.05 mv. in both cases. Etching by immersion of the crystal in dilute hydrochloric acid until the mirror-like cleavage surface had become dull was found to accelerate the rate at which the face attained the equilibrium potential but did not alter this potential within the limits of reproducibility for initially unetched crystals. Similarly a crystal which had attained the equilibrium potential by immersion for twenty-four to forty-eight hours in the electrolyte and then been withdrawn into the cell vestibule required less than an hour to reach the equilibrium value after re-immersion. Initial potentials observed immediately after introduction of an unetched cleavage surface into the electrolyte were consistently lower than the equilibrium potential and rose slowly, the more slowly the more dilute the electrolyte, until the equilibrium value was attained.

Discussion of Results

The conclusion of primary importance to be drawn from this work is that of the constancy and reproducibility of the equilibrium potential of single zinc crystals when an isolated area of a (0001) face is presented to the electrolyte, a result essential to further work bearing on the question of the variation of potential with orientation and on the study of the surface structure of crystals by measurement of non-equilibrium potentials. A further conclusion is that this equilibrium potential is very nearly equal, if not identical, to that of electrolytically prepared matrix electrodes. A comparison of the measurements on crystal X-5 with those on X-3 indicates that the potential is relatively insensitive to the presence of impurities in the zinc from which a crystal is made—a result to be anticipated from the known fact that during the growth of a single crystal impurities are thrown out at the crystal boundaries—and comparison of X-5 with all the other crystals indicates that the potential is not affected by the slight mechanical deformation attending the cleaving process. Finally, the measurements on crystal X-6 show that a rod which is a cylindrical section of a crystal parallel to its major axis and which contains along with the (0001) face sharp edges and orientations other than the (0001) gives the same equilibrium potential as the isolated basal plane.

These results when considered in conjunction with the probable potential energies associated with the various possible positions of atoms on the surface of a zinc lattice permit us to draw certain tentative conclusions regarding the significance of the equilibrium potential. Kossel,[6] with a view to explaining the mechanism of crystal growth, has recently calculated for the cubic ionic lattice of sodium chloride the potential energy changes attending the addition or removal of an ion at the surfaces, edges and corners of this crystal. Similar calculations cannot be carried out at present for an atomic metal lattice but it seems probable that the relation of potential energy to lattice position in such lattices will be found to parallel that in the ionic lattice. If this parallelism be assumed, we may draw up a table of the relative energies required to remove an atom of zinc as a function of the position of the atom in the region of the (0001) lattice face. Position I requires the maximum, (7) the minimum energy for removal of an atom

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[6] (a) Kossel, *Gott. Nach.*, 135 (1927); (b) *Metallwirtschaft*, 36, 877 (1929); also (c) Stranski, *Jahrb. d. Univ. Sofia*, 24, 297 (1927–1928); (d) *Z. physik. Chem.*, 136, 259 (1928).

(1) Unbroken (0001) surface layer
(2) Edge of perfect crystal
(3) Corner of perfect crystal
(4) Surface layer broken to depth of one atom layer; the "repeatable step" corresponding to the lattice energy
(5) Isolated atom projecting from a corner
(6) Isolated atom projecting from an edge
(7) Isolated atom projecting from an unbroken (0001) surface layer

The hexagonal symmetry of the zinc lattice would be expected to alter the absolute values for the edge and corner energies calculated for a cubic lattice but probably would not affect relative positions in this series.

The relation of this result to the free energies measurable by electrode potentials may be obtained by thermodynamic analysis of the electrode reaction into four primary reactions representing the elementary processes involved

$$\begin{array}{rll}
\text{Zn (lattice)} & \longrightarrow \text{Zn (gas)} + \Delta H_1 & (1)\\
\text{Zn (gas)} & \longrightarrow \text{Zn}^{++}\text{ (gas)} + 2\text{E (gas)} + \Delta H_2 & (2)\\
\text{Zn}^{++}\text{ (gas)} & \longrightarrow \text{Zn}^{++}\text{ (solution)} - \Delta H_3 & (3)\\
2\text{E (gas)} & \longrightarrow 2\text{E (lattice)} - \Delta H_4 & (4)\\
\hline
\text{Zn (lattice)} & \longrightarrow \text{Zn}^{++}\text{ (solution)} + 2\text{E (lattice)} + \Delta H_5 & (5)
\end{array}$$

$$(-\Delta H_5) = -\Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4 = (-\Delta F_5) + T\,\mathrm{d}\Delta F_5/\mathrm{d}T$$

Reactions 2 and 3 representing, respectively, the ionization of zinc vapor and the solution of gaseous zinc ion are independent of the electrode structure. ΔH_1, the heat of sublimation, would be expected to vary with atomic position in accordance with the postulated energy series provided a sufficient number of similarly situated atoms are present to insure the validity of statistical laws. The evaluation of ΔF_5 involves the absolute potential of the hydrogen electrode, which is not definitely known, but this difficulty does not arise in considering the variations in ΔF_5. The correlation of variations in ΔF_5 with atomic position with the corresponding variations in ΔH_1 requires a knowledge of the variation of the heat of the single electrode reaction 5 and of the variation of the heat of condensation of electrons with the arrangement of atoms on a crystal face, neither of which can be evaluated at present; we may, however, as a working hypothesis tentatively assume that the variations in the potential energy of atomic position are paralleled by variations in ΔF_5, a relatively low value of the potential energy—or high energy of removal—corresponding to a high ΔH_1, a numerically low $(-\Delta F_5)$, and a low electrode potential. On this basis it would be predicted that the potential of the unbroken (0001) face of a single zinc crystal should be a minimum and the potential of isolated atoms of zinc "adsorbed" on this surface *a* maximum, while the potential corresponding to the stepwise growth or disintegration of the crystal should be intermediate between these extreme values. It would be predicted that in contact with an electrolyte isolated atoms with a high potential energy should rapidly disappear and we might be led to expect that final equilibrium would be established when the crystal presents an unbroken **(0001)** face to the electrolyte, in accord with the principle of minimum energy developed in particular by Stranski.[6d] It would seem probable, on the other hand, that in the purest crystal and electrolyte which can be prepared, there must still be present traces of impurities sufficient to prevent the formation of the ideal surface structure.[7] Our experimental results are consistent in indicating that the surface structure of crystals which have attained the equilibrium potential is broken rather than regular. The effect of etching in accelerating the rate of attainment of equilibrium, the fact that a crystal in attaining the equilibrium potential seems invariably to lose its mirror-like appearance, the stability of potential of these etched surfaces over long periods of time, and the results for crystal sections all seem to point, furthermore, to the conclusion that the equilibrium potential must be identified with the process of stepwise growth of the crystal, that it measures the energy of the "repeatable step." This energy is independent of orientation and the equilibrium potential cannot, therefore, be assigned to any crystal face.

The significance of the fact that the initial potential measured when a crystal is brought into contact with the electrolyte is consistently lower than the equilibrium value is not clear; the most obvious explanation that this effect is due to gases dissolved in the crystal surface which slowly diffuse into the electrolyte is met by the difficulty that crystals which have once come to equilibrium with the electrolyte attain this equilibrium again in a relatively short time, in some cases within a few minutes, after they have been taken out into the air and then re-immersed in the electrolyte. Electrolytic crystals which have been exposed to hydrogen as well as to air exhibit similarly low initial potentials. Other possible explanations involve a re-arrangement of the crystal surface layer in favor of the stepwise structure or the formation of stable layers of adsorbed ions or a combination of these processes leading to final equilibrium at the interfaces of the system basic crystal lattice–surface region of lattice–adsorbed ion layer–homogeneous electrolyte. It may be pointed out, in any case, that if our interpretation of the electrode potential is valid, the estimation of the potentials of individual crystal faces, if possible at all, must be obtained from a study of these initial, non-equilibrium potentials. Measurements of this nature now in progress indicate that the initial potential observed when an unetched **(0001)** face is brought into contact with an electrolyte of **0.02** M zinc chloride in a nitrogen atmosphere is reproducible to within a few millivolts or within **10%** of the difference between the initial and equilibrium

[7] The conclusion of Zwicky, *Proc. Nat. Acad. Sci.*, 15, 253 (1929), that even the ideal crystal surface contains regularly spaced sub-microscopic crevices is of interest in this connection.

potentials. It should be of particular interest to determine the initial potentials for one or more naturally developed faces other than the (0001). Attempts to obtain prismatic or pyramidal faces by cleavage at liquid-air temperature have failed and measurements on mechanically cut sections have been abandoned as inconsistent; annealing sufficiently thorough to remove the effects of deformation during the cutting apparently induces recrystallization in the surface layer, the equilibrium potential is found to be identical to that of the (0001) face, and the initial potentials though showing some regularity are not sufficiently reproducible to allow of drawing any reliable conclusions regarding a variation of potential with orientation. In the light of our interpretation of the significance of the equilibrium potential, it appears probable that the measurements of Straumanis,[8] which are presumably for the equilibrium state, are without significance as regards the orientation–potential question. It seems essential that a method of growing, single metal crystals with naturally developed faces be devised and work on this problem is in progress.

I should like to record my great obligation to Professor P. W. Bridgman for his interest and advice during the course of this work.

Summary

1. Examination of the electromotive characteristics of single metal crystals is suggested as a means of determining the relation of potentials to definitely describable surface structures and of contributing thereby to the study of the mechanism of electrode reactions and of the complementary problem of metallic surface structure.

2. Single zinc crystals are found to behave as reversible electrodes; the (0001) cleavage face measured in air-free cells of type: Zn, $ZnCl_2$ (0.5 M), HgCl, Hg is capable of yielding potentials constant to ±0.02 millivolt and reproducible over dissimilarly prepared crystals to ±0.1 millivolt.

3. The significance of the equilibrium potential is considered in the light of Kossel's calculation of the potential energy of atoms at the various possible positions on a crystal surface. It is concluded that this potential is to be assigned to the "repeatable step" in the growth or disintegration of the crystal.

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[8] Straumanis, Nature, July 13, 1929; *cf.* Anderson, *ibid.*, January 12, 1929

NOTES

The Effect of Ions on Sedimentation of Colloidal Particles by Means of the Centrifuge.—It is sometimes assumed that the ease of removal of colloidal particles by means of the centrifuge is a measure of the size and density of the colloidal particle, but with ionizing solvents this may not be the case. We have noticed that the Sharples turbine-driven Laboratory Centrifuge with a centrifugal force of 40,000 times gravity will sometimes remove much dissolved hemoglobin (even from alkaline solutions) if the sample is centrifuged for twelve hours, while at other times the same treatment will not even remove a heavy opacity due to relatively large particles suspended in water.

This difficulty was at first believed to be due to convection currents, for Svedberg[1] ran his "ultracentrifuge" for sedimenting dissolved proteins (giving 90,000 times gravity) in an atmosphere of hydrogen under greatly reduced pressure to avoid convection currents. We reduced this difficulty by running the bowl at about 4°, where the density of water does not change with the temperature. For this purpose the shielding jacket and upper "cover" of the centrifuge are cooled with brine at about −10°. The 14° temperature difference is maintained by friction in the air surrounding the bowl. This air is at the same temperature as the bowl, so that the temperature gradient appears to be entirely in the iron shielding jacket and at its surfaces. For such purposes the jacket should be thinner, or even better, of copper rather than cast iron.

The maximum density of water is not much affected by salts. For example, 0.5 N sodium chloride lowers the temperature of the maximum density of water by 6.6°, this being a typical value, and the effect being for a particular salt nearly proportional to the concentration of that salt.[2]

A simple calculation shows that the difficulty could well be electrical. Suppose that at a distance h from the axis of the centrifuge the force is L times the force of gravity, g, that the concn. of ion No. 1 is c_1 moles per liter, that the ion has molecular weight M_1, partial molal volume[3] $\overline{V}_1$ and n_1 equivalents of positive electricity per mole (n_1 being either positive or negative). Let the electrical potential be E volts; R is the gas constant and ρ the density of the solution (not of the solvent); T the absolute temperature, and ln means "natural logarithm." We have, using absolute c. g. s. units and the usual differential notation, and assuming activity to be equal to concentration[4]

$$RT\,\mathrm{d}\ln c_1/\mathrm{d}h = gL(M_1 - \rho\overline{V}_1) - 96{,}494 \times 10^7\, n_1\, \mathrm{d}E/\mathrm{d}h \qquad (1)$$

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[1] Svedberg, *Z. physik. Chem.*, **121**, 65 (1926); **127**, 51 (1927).

[2] Landolt-Bornstein, "Physikalisch-chemische Tabellen," **1923**, Vol. I, **p.** 439.

[3] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 204.

[4] Compare Lewis and Randall, Ref. **3**, p. 244.

We define ρ_1 as $M_1/\overline{V}_1$ and define the "buoyancy coefficient," r_1 by

$$M_1 - \rho\overline{V}_1 = M_1\,(1 - \rho/\rho_1) = M_1r_1 \qquad (2)$$

We have for the various ions present the quantities c_2, c_3, c_4, etc., respectively, each ion giving an Equation 1 and an Equation 2. Also we must have for all the ions together, for any value of h whatever

$$n_1c_1 + n_2c_2 + n_3c_3 + \ldots = \Sigma(nc) = 0 \qquad (3)$$

Combining (1) and (2) for each ion with the derivative of **(3)** with respect to h, and remembering that d In $x/\mathrm{d}x = 1/x$, we solve for E and find

$$RT\,d\ln c_1/\mathrm{d}h = gL[M_1r_1 - n_1\Sigma(Mrnc)/\Sigma(n^2c)] \qquad (4)$$

the summations extending over all the ions. We write for each separate ion an equation of the type $I_1 = n_1^2c_1/2$, where I_1 is the "ionic strength" of that ion.[5] (4) may now be written

$$RT\,d\ln c_1/gL\,dh = M_1r_1(\Sigma I - I_1)/\Sigma I - n_1[\Sigma(Mrnc) - M_1r_1n_1c_1]/2\Sigma I \qquad (5)$$

The equivalent of this formula has been given[6] for the case where there are but two kinds of charged ions (including the charged colloid). Svedberg's formula takes account of the sedimenting effect of heavy ions only when the effect of those on the density of his original un-ionized colloid is considered. Colby, Des Coudres and Tolman[7] have each given theoretical and experimental treatment of centrifugal potentials in electrolytes. They assume no concentration gradient, and accordingly their potential differs from ours by a concentration cell potential. As the latter involves transference numbers,[8] we see how these three observers could obtain transference numbers, although our potential of Equation 1 does not involve transference numbers.

The first term on the right of (5) involves the pull on ion No. 1 only, while the second term involves the centrifugal pull on all the other ions. For an uncharged substance the second term vanishes as n_1 is 0.

An efficient centrifugal process may use either or both of the two terms. Consider the first only, for a protein of density about 1.25,[9] whence $r_1 = (1.25 - 1)/1.25 = 0.2$ approx. (This should not presumably be affected by "swelling," although the time of reaching equilibrium may be enormously increased thereby.) Assume a 1% solution of this protein with molecular weight 40,000 and an equivalent weight of 1000 toward sodium hydroxide and assume the sodium salt to have been obtained by adding sufficient sodium hydroxide. We have $c_1 = 10/40{,}000 = 0.00025$ mole per liter, and $n_1 = 40$, whence $I_1 = {}^1/_2 \times 40^2 \times 0.00025 = 0.2$. But the ionic strength due to sodium ion is only $40 \times 0.00025/2 = 0.005$. Hence the

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[5] Lewis *and Randall, Ref.* **3, p. 373.**

[6] *Svedberg, Kolloid-Z., Erganzungsband* **zu, 36,** 63 **(1925).**

[7] **Tolman,** THIS **JOURNAL, 33,** *121 (1911).*

[8] *See Lewis and Randall, Ref.* **3, p. 338.**

[9] *See Svedberg, Z. physik.* ***Chem.,*** **121,** 65 *(1926).*

concentration gradient attainable will be only 0.005/0.205 or 1/41 (*i. e.*, $1/(n_1 + 1)$ that attainable by also adding salt to the solution). We may remark that association in this alkaline solution is of no avail. Supposing groups of 10 molecules of protein to associate, giving a molecular weight of 400,000, we have now a factor of 1/401 by which this is to be multiplied, for the association does not presumably change the equivalent weight toward sodium hydroxide. But association will naturally decrease the *time* of attaining equilibrium. In this particular case salt (or excess sodium hydroxide) might be added to an additional ionic strength of somewhat more than 0.2, for maximum efficiency. It is to be noted that the removal of the protein has the same effect on the efficiency as the addition of salt, so that if enough salt is present for the particles to really start to be sedimented, the process might be expected to continue with increasing efficiency.

To illustrate the second right-hand term of (5) we may suppose that to the above alkaline 1% protein solution is added 0.1 mole of thallous sulfate per liter of solution, giving an additional ionic strength of 0.3. Owing to its low weight and density we neglect the sedimenting effect of the SO_4^{--}, and take for Tl^+ the approximate atomic weight 200, also $r = 1$ approximately for this heavy ion. We have then neglecting the Na^+ present

$$RT\,d\ln c_1/dh = gL[40{,}000 \times 0.2(0.5 - 0.2)/0.5 - (-40) \times 200 \times 0.2/2 \times 0.51 = gL(4800 + 1600)$$

Evidently simple ions like Tl^+ do not enormously affect the second term, the increase due to the weight of the Tl^+ (as against an equivalent amount of, say sodium or ammonium sulfate) being here about $33^1/_3$%. The total effect is 6400/(40,000 × 0.2/41) or 32.8 times that where no salt whatever is added, but is 6400/40,000 × 0.2 or 0.8 times that attainable at the isoelectric point. We may note that at the isoelectric point the effect of ions must entirely disappear, and speaking roughly is proportionately greater the farther the protein is from its isoelectric point.

Some improvement is obtained in the second term by using a *monovalent* negative ion with the Tl^+. There are available certain heavy *negative* ions such as phosphotungstate and phosphomolybdate ions, *e.* g., as one with 24 gram-atoms or 2304 g. of molybdenum metal per mole, and if intelligently used such an ion might be equivalent to a ten-fold increase in the force of the centrifuge. The virtues of such ions are well known. These ions will be a disadvantage for a negatively charged colloid, unless enough should be added to cause the colloid to rise rather than sink.

Summary

It is shown how the intelligent use of salts may enormously affect the efficiency of centrifugal processes in ionizing solvents, apart from any

possible agglutination, association or chemical combination caused by the added salt.

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Note on the Magnetic Susceptibility of the Manganocyanide Ion.—We had occasion to make a rough determination of the susceptibility of the manganocyanide ion. The method employed was the Gouy[1] method, so modified as to eliminate most of the pull due to the water. The upper compartment was kept filled with a solution of manganous sulfate 0.058 molal, and the lower, in the first instance, open to the atmosphere. In the second series of runs the lower compartment was filled with a solution of the same concentration of manganous ion in the presence of 2.3 *M* potassium cyanide.

The solution was so prepared as to avoid the oxidation of the manganocyanide by the oxygen of the air. This was done by using xylene for covering.

The diamagnetic susceptibility of the potassium cyanide was determined in a separate run, thus making our determination of the susceptibility of the manganocyanide independent of the impurities in the potassium cyanide. The densities of the solutions were determined to 0.1%. The sample of manganous sulfate was of high purity (containing 0.001% of iron).

Employing the values of the magnetic susceptibility for air, water and Cabrera's[2] value for manganous sulfate, we have calculated the susceptibility of the manganocyanide ion. This value, corrected for the total cyanide is 1650×10^{-6}. The presence of the sulfate was also corrected for; -37×10^{-6} was taken for its molal susceptibility.

It is to be noted that this value (1650×10^{-6}) lies between one (1300×10^{-6}) and two (3300×10^{-6}) Bohr magnetons if S levels are assumed. This is to be expected since this ion is iso-electronic with ferricyanide ion, which has a susceptibility of about 1700×10^{-6}. According to the Welo-Baudisch[3] rule, the manganocyanide $Mn(CN)_6^{----}$ (as well as the ferricyanide $Fe(CN)_6^{---}$) would have a susceptibility of one Bohr magneton. The deviation from one Bohr magneton in this case is in the same direction and same order of magnitude as in the case of the ferricyanide. However, it is possible to ascribe the deviation in our case as due to bivalent manganese

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[1] Shaffer and Taylor, THIS JOURNAL, 48, 843 (1926).

[2] Cabrera, Moles and Marquinas, *J. chim. phys.*, 16, 11 (1918).

[3] Welo-Baudisch, Nature, 116, 606 (1925)

in other cyanide complexes, which are known to exist. The accuracy of the determination is within 5%.

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THE ACTION OF SODIUM HYDROXIDE ON CELLULOSE

BY J. S. RUMBOLD

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Introduction

When a sample of cellulose is steeped in an aqueous solution of sodium hydroxide, the concentration of the sodium hydroxide is diminished by an amount which depends on the temperature and the concentration. Some of the previous work on the mechanism of this interesting effect has been summarized recently by G. W. Blanco.[1] The evidence seems to favor the explanation which assumes the formation of a compound, but although many investigators agree that above a concentration of 16% the amount of caustic alkali absorbed by a given weight of cellulose is constant, the literature contains a remarkable variety of curves for the absorption from the more dilute solutions.

Cellulose is a very variable material, and the discrepancy between the results obtained by different investigators suggests that the absorption from dilute solutions may be a physical rather than a chemical process. It was, therefore, thought desirable to attempt to correlate absorption of sodium hydroxide from dilute solutions and certain physical properties of the cellulose. No results have yet been obtained from work in this direction since most of the celluloses selected for the purpose were found to be unsuitable on account of unexpected difficulties in filtration, and the present work is confined to a highly resistant cotton cellulose. The results so far indicate that there is a chemical reaction between cellulose and sodium hydroxide even when the latter is present in dilute solution. However, experiments are being continued with other varieties of cellulose, and it is hoped to deal with these in a later paper.

Description and Preparation of Materials.—The moisture content of the cotton, determined by heating to constant weight at 100°, was 6.96%, and the ash content was 0.035%. Its resistance to the peptizing action of strong alkali indicated that it was probably free from the organic impurities present in certain other celluloses, and except for a trace of ammonia no detectable amount of impurity could be removed by washing

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[1] Blanco, Ind. *Eng. Chem.*, **20**, 926 (1928).

it with water or hydrochloric acid. It was, therefore, considered pure enough to be used without preliminary treatment. In order to obtain a uniform moisture content, enough for the whole investigation was stored for several weeks in an air-tight bottle and the moisture content was checked from time to time during the course of the work; the variation was negligible.

The sodium hydroxide solutions were made from sodium in a platinum dish and usually gave no reaction for carbonate, although some contained a trace; all were free from sulfate and chloride. They were always prepared immediately before they were required.

Determination of the Sodium Hydroxide Absorbed.—To determine the concentration of the sodium hydroxide solutions, portions were measured from weight burets into platinum dishes, slightly acidified with hydrochloric acid and evaporated to dryness in an oven at 100°. The residues were heated for one to two hours at 250° and then at 650° in an electric furnace in covered dishes to constant weight. When the work was almost complete, a paper by Richards and Hall[2] appeared in which it was concluded that nothing short of fusion would yield the anhydrous salt. The residues, of course, could not be fused, since loss by vaporization would result; to decide the matter weighed amounts of pure anhydrous sodium chloride were dissolved in water, made slightly acid with hydrochloric acid, and then treated exactly as described. In no case did the weight of residue differ by more than one unit in the fourth place from the weight of anhydrous salt, and it was concluded that a final treatment at 650° is as effective as a fusion in removing the last trace of moisture. The residues lost 0.15 to 0.20% of their weight by the heating in the electric furnace.

Each absorption experiment was carried out in the following way. Weighed amounts of solution and cotton were placed in a test-tube, which was then closed by a rubber stopper and well shaken. The contents of the test-tube were transferred to a Gooch crucible, in which the cotton was pressed to form a compact filtering medium, and the solution was poured through two or three times. The filtration seldom occupied more than a minute or two, so that it was unnecessary to take special precautions to protect the solution from contact with the carbon dioxide of the air. The filtrate was then analyzed by the method described above.

The amount of sodium hydroxide absorbed was calculated as follows. Let W = weight of original solution, w = weight of sodium hydroxide which it contains and a = weight of sodium hydroxide absorbed. Then, if an amount W' of the filtrate is found by analysis to contain w' of sodium hydroxide, $W - a = (w - a)(W'/w')$; and hence $a = (wW' - w'W)/(W' - w')$. The same amount of cotton was not used for each experiment, but usually about 0.4 g. was treated with 50 to 60 g. of solution. After removal of the cotton, about 30 g. was employed to determine w'.

The last trace of cotton could not be removed by the method of filtration; the amount which passed into the filtrate slightly increased with increase in concentration of sodium hydroxide. Since it was never more than a trace, and was completely burned in the treatment of the sodium chloride residues, no importance was attached to it.

The Effect of Time.—It has been previously shown[3] that equilibrium

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[2] Richards and Hall, This Journal, 51, 709 (1929).

[3] Karrer, *Cellulosechemie*, 2, 216 (1921); Dehnert, *ibid.*, 5, 19 (1924); Liepatoff, *Kolloid-Z.*, 36, 149 (1925).

is established very rapidly. A number of determinations were made in which the time of contact of the cotton with the solution was varied. For periods longer than half an hour, weighed amounts of solution and cotton were placed in paraffined test-tubes, which were than sealed and left in a thermostat for the desired time. The same amount of cotton and as nearly as possible the same amount of solution were used for each experiment of a series.

It appears from the results given in Table I that the time of contact, beyond a few minutes, has practically no influence on the absorption; and in subsequent determinations the cotton was well shaken with the solution, allowed to stand for a few minutes, and then removed.

TABLE I

EFFECT OF TIME ON THE AMOUNT OF SODIUM HYDROXIDE ABSORBED BY ONE GRAM OF COTTON AT 20°

Time, hours	Final concn. of NaOH, g. per 100 g. of soln.	NaOH absorbed by 1 g. of cotton, g.	Time, hours	Final concn. of NaOH, g. per 100 g. of soln.	NaOH absorbed by 1 g. of cotton, g.
Series 1. (Initial concn. of NaOH, 8.103 g. per 100 g. of soln.)			Series 3. (Initial concn. of NaOH, 4.952 g. per 100 g. of soln.)		
0.05	8.074	0.0240	0.05	4.912	0.0209
2.5	8.077	.0234	.5	4.909	.0210
64.0	8.076	.0240	63.0	4.911	.0206
Series 2. (Initial concn. of NaOH, 3.631 g. per 100 g. of soln.)			Series 4. (Initial concn. of NaOH, 2.011 g. per 100 g. of soln.)		
0.5	3.610	0.0206	4.75	2.005	0.0061
14.5	3.608	.0204	20.0	2.005	.0059
42.0	3.607	.0204	73.0	2.003	.0054

The Effect of Mercerization.—Preliminary experiments showed that over the concentration range 4 to 8% the absorption was practically constant, but a relatively large increase occurred when the concentration of alkali was raised to 11%. It seemed desirable to attempt to determine whether the absorptive power of the cotton had been irreversibly increased by treatment with alkali of this concentration.

Samples were, therefore, steeped in solutions of various strengths up to 30% and washed free of alkali. The cotton which had been treated with the more concentrated solutions showed a marked increase in absorptive power. The data, plotted as curves in Fig. 1, show that previous treatment with 5% alkali has no effect on the power of absorption, but stronger solutions cause an apparently permanent increase, which reaches a maximum when the concentration of the modifying solution is about 20%.

These results may be correlated with those of x-ray investigations of cellulose. Katz[4] found that the x-ray spectrum of mercerized cotton differs from that of native cotton, but this effect is not produced when

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[4] Katz, *Z. Electrochem.*, 32, 273 (1926).

alkali of concentration less than 8% is used. Meyer and Mark[5] have shown that mercerization causes an increase in the volume of the space lattice, which is explained by a spatial rearrangement of the parallel cellobiose chains. It is assumed that the chains are held together laterally by secondary valences, and that the broadening of the space lattice is accompanied by a weakening of these micellar forces and a corresponding increase in the reactivity of the cellulose. The latter authors point out that the strong inter-micellar forces are probably due to the attraction of the (OH) groups. With these assumptions it might be expected that the increase in the volume of the space lattice, produced by the action of the more concentrated solutions, would result in a stronger attraction for sodium hydroxide. Further, the weakening of the inter-micellar forces is probably brought about by penetration of the space lattice by the alkali; and it may be supposed that up to a concentration of 5% the amount of absorbed alkali is insufficient to produce a permanent distortion of the lattice.

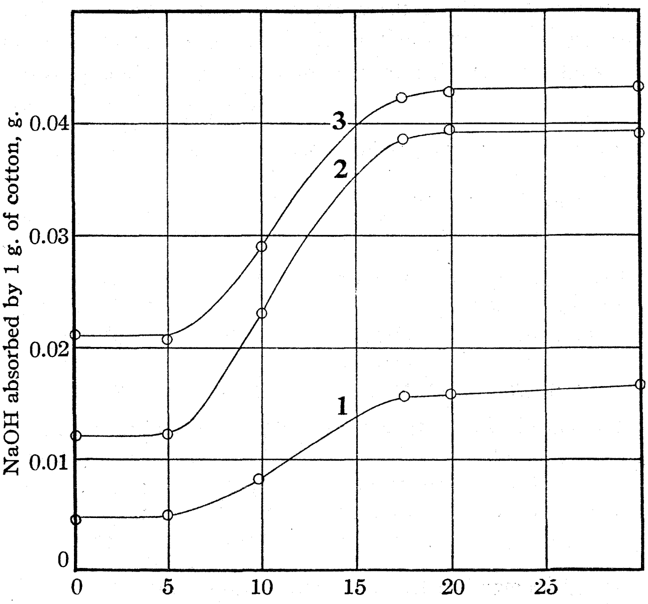

Fig. 1.—Absorption of NaOH by cotton at 20° after preliminary treatment with NaOH solution.

In order to study the action of dilute alkali on the mercerized product, about 20 g. was prepared from the native cotton by means of a 20% mercerizing solution, and the absorption of sodium hydroxide from solutions of various strengths was determined in the manner previously described.

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[5] Meyer and Mark, Ber., 61,593 (1928).

Results and Conclusions

The experimental results are shown graphically in Fig. 2. The most striking point about the curves is the presence of the "breaks," which occur in both when the concentration is about 4%. At this concentration the compositions of the absorption complex are almost exactly expressed by $(C_6H_{10}O_5)_{12}\cdot NaOH$ (calcd., 0.0206 g. of NaOH per gram of cellulose) for the native cotton, and $(C_6H_{10}O_5)_{12}\cdot 2NaOH$ (calcd. 0.0412 g. of NaOH per gram of cellulose) for the mercerized cotton. The general character of the curves shows that the effect is not one of adsorption; and it is, therefore, improbable that the imbibition by the cotton takes place between colloidal particles. Moreover, the profound modification produced by the action of concentrated alkali indicates that an intimate penetration of the cellulose occurs, and there is no reason to suppose that the penetration of the lattice is confined to a particular concentration range. The speed with which equilibrium is attained is, however, not in accordance with the formation of solid solutions, and it is concluded that the absorption is a chemical process analogous to the formation of molecular com-

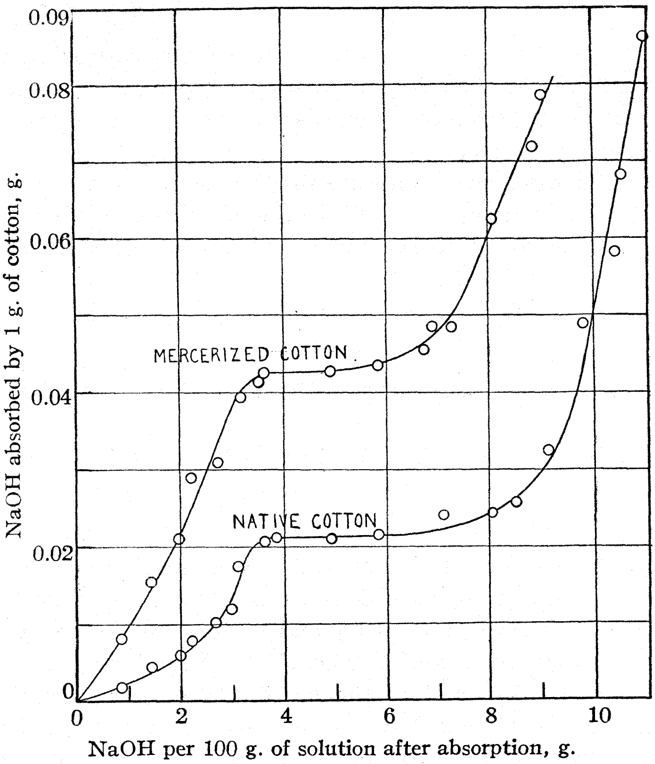

Fig. 2.—Absorption of sodium hydroxide by cotton.

pounds. According to this view, the horizontal parts of the curves indicate that the residual fields present in the cellulose are temporarily neutralized by the formation of the compounds $(C_6H_{10}O_5)_{12}\cdot NaOH$ from native cotton and $(C_6H_{10}O_5)_{12}\cdot 2NaOH$ from mercerized cotton.

Summary

1. The absorption of sodium hydroxide by cotton has been shown to take place very rapidly, and to change only slightly over a period of two or three days.

2. Previous treatment of the cotton by sodium hydroxide solution of concentration greater than 5% increases its power of absorption. The maximum effect is produced when the concentration of the modifying solution is 20% or greater.

3. The absorption curves indicate that the action of sodium hydroxide solution of concentration 4 to 5% is the formation of the compounds $(C_6H_{10}O_5)_{12}\cdot NaOH$ from native cotton and $(C_6H_{10}O_5)_{12}\cdot 2NaOH$ from mercerized cotton.

GRAND FALLS, NEWFOUNDLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

A NEW METHOD OF PREPARING ACETALS

BY J. A. NIEUWLAND, R. R. VOGT AND W. L. FOOHEY

RECEIVED MAY 16, 1929 PUBLISHED MARCH 6, 1930

Boron and silicon fluorides react readily with methyl or ethyl alcohols, forming heavy, fuming, almost colorless, and strongly acid liquids. These solutions have been studied by Liebig and Wöhler,[1] W. Knop,[2] Gay-Lussac and Thénard,[3] Kuhlman,[4] and V. Gasselin.[5] Due, however, to the complexity of the mixtures and to the instability of the compounds when isolated, the acids present have never been definitely identified. By distilling a solution of one mole of boron fluoride in one mole of methyl alcohol, Gasselin obtained an acid residue and the neutral compounds CH_3OBF_2 and $(CH_3O)_2BF$; but these in turn are decomposed by more alcohol with the liberation of acid. In the case of boron fluoride, the acid is probably HBF_4, or possibly H_3BF_6 or an ester acid, dissolved and ionized in absolute alcohol or some other constituent of the mixture. Orthoboric ester, which may be present, was shown by Walden[6] to be a

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[1] Liebig and Wöhler, Pogg. *Ann.*. 24, 171 (1832).

[2] W. Knop, J. *prakt. Chem.*, [1] 74, 41 (1858).

[3] Gay-Lussac and Thénard, "Recherches physico-chimiques," Vol. II, p. 39.

[4] Kuhlman, *Ann.*, 33, 205 (1840).

[5] V. Gasselin, *Ann. chim. phys.*, [7] 3, 5–83 (1894).

[6] Walden, *Z. physik. Chem.*, 54, 175 (1906).

good ionizing solvent; or CH_3OBF_2 and $(CH_3O)_2BF$ which are the fluorine derivatives of the ester may act in this way. Silicon fluoride apparently produces similar solutions of H_2SiF_6. Gases having the properties of diborane and silicane are formed on treating these solutions with a metal such as iron, zinc, magnesium or aluminum.

We have found these acids, especially the boron fluoride solution in methyl alcohol, to be much superior to sulfuric or any other acid in making ethylidene compounds from acetylene with mercuric oxide as catalyst. They did not attack glass, dissolved mercuric oxide readily, were lasting and effective in very low concentration, prolonged the usefulness of the mercury and formed only traces of tarry by-products. They did not remove halogens, ether or ester groups from compounds treated, and were easily separated from the finished product. By their use we have been able to prepare a number of new ethylidene ethers or acetals which could not be obtained from acetylene in the presence of sulfuric acid or by any other known process. These acids in the presence of mercuric oxide caused acetylene to combine with strong organic acids, alcohols, glycols, hydroxy acids, β-diketones and phenols, etc. The silicon fluoride solution especially, formed compounds with phenols, differing markedly from those produced in sulfuric acid. In reactions of acetylene with aryl hydrocarbons and phenolic ethers, these acids did not seem to be effective.

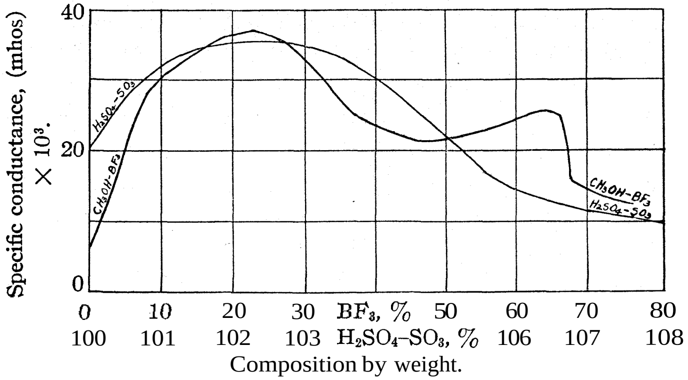


Fig. 1.—Specific conductance of the systems CH_3OH–BF_3 and H_2SO_4–SO_3.

Although boron or silicon fluorides passed directly into many organic hydroxyl compounds formed acid solutions and acted with mercuric oxide as catalysts for acetylene, it was found more convenient to make up a stock solution in methyl alcohol. A *55–73%* solution of boron fluoride was generally used. The graph of the specific conductance of such a solution as compared with **sulfuric** acid indicated that it contained a strong non-aqueous acid (Fig. 1). The compound $BF_3 \cdot (C_2H_5)_2O$ (b. p. 124°)

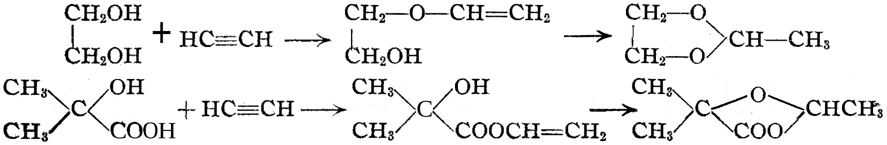
prepared from boron fluoride and ether could also serve as a catalyst, in which case the ether was liberated by the reacting compounds, and should be swept from the system by a stream of acetylene as free ether; when present in quantity it retarded catalysis in the alcoholic solution. Methyl alcohol dissolved only 37 parts by weight of silicon fluoride.

The reactions for the union of boron trifluoride and alcohol may perhaps be written according to the following scheme. Fluo acids may be present as shown by the conductive curve and the quantities of boron trifluoride absorbed by the alcohol at the concentrations when the curve has two maxima.

$$(4BF_3 + 3CH_3OH \longrightarrow (CH_3O)_3B + 3HBF_4)$$
$$BF_3 + 2(CH_3O)_3B \longrightarrow 3(CH_3O)_2BF$$
$$BF_3 + (CH_3O)_2BF \longrightarrow 2(CH_3O)BF_2$$
$$\text{also } (2BF_3 + 3CH_3OH \longrightarrow H_3BF_6 + (CH_3O)_3B), \text{ etc.}$$

I. Acetals of Glycols, Oxy-acids and Other Derivatives.—Several acetals have previously been prepared by the action of acetylene on alcohols in the presence of mercuric sulfate and sulfuric acid by Nieuwland and co-workers.[7] Hill and Hibbert[8] obtained a series of cyclic acetals from glycols by a somewhat similar method.

Using the alcoholic solutions of boron or silicon fluorides with mercuric oxide as catalysts, we have prepared from acetylene the acetals of polyhydric alcohols and of their ethers, chlorohydrins and of the hydroxy acids and their esters. All of these reactions are presumed to take place in two steps;[9] (a) addition of acetylene to form a vinyl ether, (b) spontaneous change of the vinyl ether to the acetal in acid solutions by rearrangement in the case of polyhydric alcohols or by addition of a second molecule in the case of monohydric compounds, according to the following scheme of reactions



The procedure is nearly uniform for all substances treated and may be illustrated by the case of ethylidene glycol.

Experimental

Five grams of a 55–65% solution of boron fluoride in methyl alcohol was weighed into a tared flask and one gram of mercuric oxide partly dissolved in it by gentle heating. The flask was then cooled, 102 g. of ethylene glycol added and the whole well mixed. Dry acetylene from a gasometer was then passed into the closed flask with occasional

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[7] Reichert, Bailey and Nieuwland, THIS JOURNAL, 45, 1552 (1923).

[8] Hill and Hibbert, *ibid.*, 45,3108 (1923).

[9] *Cf.* Hill and Pidgeon, *ibid.*, 50,2718 (1928).

shaking until the calculated weight had been absorbed.[10] Potassium carbonate and a small quantity of water were then added to neutralize the acid and the acetal layer was separated, dried over potassium carbonate and fractionated.

Special adaptations of the procedure were made to fit certain cases. The quantity of acid required varied. A portion of glycerol acetal containing 0.142 g. of boron fluoride solution from a previous run was sufficient to catalyze **250** g. of glycerol to the acetal. One gram of mercuric oxide ordinarily would catalyze about 20 g. of acetylene to the ethylidene group, but to prevent too violent a reaction the oxide was ordinarily added in one to two-gram portions when it was needed, *e. g.*, as indicated by slow ahsorption of acetylene. A solvent, preferably ethylidene glycol, was used with some of the solids of higher melting point, such as dimethylcitric acid, benzilic acid and mandelic acid. The acetylene was catalyzed to the cthylidene group, simultaneously removing the hydrogen of the hydroxyl and carboxyl groups. The 1-hydroxy-carboxylic groups seemed to be more readily attached to form ethylidene groups than 2- or 3-hydroxy acids. Other lower melting solids such as pinacol and pentacrythritol were simply moistened with the acid mercury oxide catalytic solution and they slowly liquefied during acetal formation. In the case of viscous liquids or solids, care must be taken to avoid local overheating by cooling the reaction flask. The speed of acetylene absorption often increased as more acetal was formed due to the greater solubility of the acetylene in it. This was especially noticeable with glycerol. The reaction might be speeded by adding a portion of glycerol acetal from a previous run at the very start. When the hydroxyl groups or hydroxyl and carboxylic groups in a compound were present in even number, the absorption of acetylene stopped quantitatively when all their labile hydrogens were replaced with ethylidene group. In other cases an excess of acetylene which might combine to form more complex compounds must be avoided. Glycerol, for example, formed first ethylidene glycerol. This acetal, either in the original mixture or after separation, formed ter-ethylidene-bis-glycerol when treated with additional acetylene in the presence of the catalyst. In separating the high-boiling acetals ether was first added, then potassium carbonate and then water. The acetal ether layer was separated and dried over anhydrous potassium carbonate, and the liquids fractionated or crystallized in an appropriate solvent, preferably alcohol.

Where available, purified commercial preparations were treated to form acetals but the following substances were prepared in this laboratory: **(1)** hydroxyisobutyric acid was made by saponifying the commercial ethyl ester with sodium hydroxide, precipitating the zinc salt, treating with hydrogen sulfide and removing the water by vacuum distillation at 45°. The acid sublimed at 50°. **(2)** β-Methyl malate[11] was made by refluxing 120 g. of malic acid with methyl alcohol in a tared flask and then removing the water and alcohol by vacuum distillation. This process was repeated until the weight of the non-volatile residue had increased by **12** g. **(3)** Dimethyl citrate (symmetrical) was prepared by the method of Schroeter and Schmitz.[12]

Table I shows the ethylidene compounds prepared by this new method, their physical constants and the yields obtained.

In explanation of this table it might be said that the compounds here listed were all purified by redistillation when possible. The products from pentaerythritol and benzilic acid were recrystallized from ethyl alcohol and that from dimethyl citrate from methyl alcohol since ethyl alcohol seemed to cause partial displacement of the methyl groups by

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[10] Cf. "Organic Syntheses," Vol. IV, John Wiley and Sons, Inc., New York, 1925, p. **28.**

[11] *Cf.* Desmondesir, *Compt. rend.*, **33, 229 (1851).**

[12] Schroeter and Schmitz, Ber., **35, 2086 (1902).**

ethyl. The ethylidene glycerol described was largely the 1,2-compound separated from its isomer by fractional distillation. Benzoylation of the original mixture of ethylidene glycerols by the method of Hill and Hibbert[13] showed that it consisted of 78% of 1,2-acetal and 22% 1,3-acetal. The ethylidene methyl ethyl pinacol was a mixture of isomers that could not be separated by fractionation, probably because of the presence of several racemic and meso isomers.

TABLE I

PREPARATIVE DATA AND PHYSICAL CONSTANTS OF COMPOUNDS

Asterisks denote new compounds.

Ethylidene compound	Taken,	Yield,		B. p., °C.	d_4	n_D
	g.	g.	%			
Ethylene glycol	102	88	62	82.3	0 9702	[illegible] 3945^{24}
Trimethylene glycol	93	55	45	10%-111	0 9675^{23}	1.4160^{23}
Pinacol	...	...	...	133–134	....	......
Methylethyl pinacol*	...	...	...	150–180	....	......
Glycol methyl ether	150	77	44	87–91 (15 mm)	0 9691^{25}	1.4181^{25}
Glycol ethyl ether	300	255	74	110–114 (14 mm.)	0.9328^{25}	1.416325
Glycol butyl ether*	200	115	52	142–146 (14 mm.)	0.9072^{26}	1.4263^{26}
Diethylene glycol*	...	...	...	250 (14 mm)	....	.....
Diethylene glycol ethyl ether*	...	...	...	140–145 (14 mm.)	....	......
Glycerol	...	...	(65–75)	189–191	1.119324	1.4395^{24}
Ter-ethylidene-*bis*-glycerol	542	322	41 7	160–162 (14 mm.)	1.106724	1 4482^{20}
Glycerol methyl ether*	141	105	60	145–147	1 009824	1.4145^{24}
Glycerol ethyl ether*	...	...	...	170–171	....	......
Glycerol phenyl ether*	150	119	68	142–144 (14 mm)	(m. p. 29")	
Bis-ethylidene-pentaerythritol*	69	86	90	113 (14 mm.)	(m. p. 40°)	
Ter-ethylidene-mannite	100	67	47	165–168 (17 mm.), sublimed at 90°		
Ethylene chlorohydrin	304	250	71	106–107 (14 mm.)	....	......
Trimethylene chlorohydrin*	157	70	38	127–129 (14 mm.)	....	......
Glycerol chlorohydrin	611	543	72	147–149	1 1720^{24}	1.4410^{24}
Glycerol monoacetin*	260	153	49	91.5–92 (14 mm.) 200–201 (760 mm.)	1.1110^{26}	1.4323^{26}
Lactic acid	240	179	61	149–151	1.074^{26}	1.4120^{26}
1-Hydroxy-isobutyric acid*	148	125	71	150 ± 0.3 (745 mm)	1.0226^{28}	1.4034^{28}
Bis-ethylidene tartrate	...	...	...	122–128 (17 mm.)	....	......
Dimethyl tartrate*	184	172	81	137 ± 0.2 (16 mm)	1 2306^{27}	1 4426^{27}
Diethyl tartrate*	162	137	74	147 ± 0 5 (18 mm)	1.1408^{25}	1.143825
Methyl malate*	120	40	26	121–122 (15 mm.)	1 1975^{26}	1 4397^{26}
Ethyl malate*	118	50	30	125–130 (17 mm.)	1 121526	1.4402^{26}
Dimethyl citrate*	93	30	31	(m. p. 73°)		
Mandelic acid*	82	62	64	142–144 (14 mm.)	1.168125	1.4145^{25}
Benzilic acid*	86	64	66	198–200 (17 mm.) (m. p. 77°)		

The alkyl ester radicals could be removed from dimethyl and diethyl ethylidene tartrate by incomplete saponification, leaving ethylidene tartaric acid in solution, and extraction with ether of the excess of acetal ester. The following salts were prepared from this solution: sodium and calcium, as non-crystallizing sirups; zinc, crystalline, insoluble in water; cobalt, cadmium, copper, manganese and ammonium, soluble and crystalline; mercurous and stannic somewhat insoluble gels. The ammonium salt was the most stable. The others decomposed slowly when moist into acetaldehyde and the corresponding tartrates.

The degree of purity of some of these ethylidene compounds may be

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[13] Hill and Hibbert, THIS JOURNAL, 50, 2247 (1928); *cf.* J. P. Van Roon, *Rec. trav. chim.*, 48, 173–190 (1929).

judged by comparing the analysis in Table II with the composition calculated from the formula.

TABLE II

ANALYTICAL DATA

Ethylidene compound	Wt. taken, g.	CO_2, g.	H_2O, g.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Pound
Glycerol or-phenyl ether	0.1704	0.4206	0.1093	68.0	67.3	7.22	7.17
Glycerol monoacetin	.1610	.3109	.1065	52.5	52.7	7.50	7.40
1-Hydroxyisobutyrate	.2705	.5504	.1855	55.4	55.5	7.69	7.65
Dimethyl tartrate	.2417	.4154	.1201	47.1	46.9	5.88	5.66
Diethyl tartrate	.2675	.4971	.1657	51.7	50.8	6.90	6.93
β-Methyl malate	.1804	.3244	.0987	48.3	48.2	5.75	6.00
Dimethyl citrate	.1775	.3193	.0899	48.8	49.0	5.69	5.67
Mandelate	.1848	.4604	.0941	67.4	67.9	5.62	5.70
Benzilate	.2374	.6610	.1184	75.6	75.9	5.51	5.57

The following substances reacted with acetylene to form derivatives, presumably acetals, but special difficulties accompanied the separation or purification.

The product from 1,2-diphenylglycol gave a solid product, m. p. 107–115°, b. p. 203–206°, but attempts to crystallize it from alcohol tended to remove the ethylidene group, leaving the crystals of the glycol. Diethyleneglycol ethyl ether (carbitol) reacted very energetically and smoothly, forming a liquid acetal that could not be distilled in a vacuum in larger quantities without decomposition; since it contained glycol, this could be removed as the low-boiling acetal. A method of determining the glycol in carbitol might be used to obtain the percentage of glycol quantitatively. Glycerol dichlorohydrin formed a high-boiling liquid product. Glycerol bromohydrin would not react at all. Bromine was apparently removed, which prevented catalysis. Trimethyleneglycol acetal in very pure condition (b. p. 110") is obtained by this method in good yield.

p-Chlorophenyl-α-ether of glycerol, b. p. 173–175° at 17 mm., and also the *o*-chloro ether could not be crystallized. *o*-Cresyl glycerol ether (b. p. 165–167° at 17 mm.) and also the *p*-cresyl ether were non-crystallizable liquids.

Diethyl racemate reacted as readily as the tartrate. The physical constants approached those of the tartrate. Diethyl mesotartrate (b. p. 135–138° at 17 mm., n_D 1.4433) is a liquid.

2,2,2-Hydroxydiphenylpropionic acid (b. p. 181–183° at 10 mm.) reacted smoothly but the isolation of the compound could not be uniformly repeated. Diethyl citrate also reacted with acetylene but the product could not be isolated. Glucose cyclo-acetoacetic ester[14] formed a solid compound, boiling at 195° at 5-6 mm., but rapidly decomposed during crystallization.

It is peculiar that glycolic acid does not react and that its presence prevents the reaction of other compounds that do form acetals in its absence. It seemed to have as marked an anticatalytic effect as that of the presence of halogen ions. Quite a number of other glycols and hydroxy acids, as well as derivatives of these, gave smooth reactions with acetylene, but the compounds were not isolated since special difficulties were encountered in their purification. We may conclude, however, that this method of making acetals may be considered to be quite general and practical in application.

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[14] E. S. West, *J. Biol. Chem.*, 74, 562 (1927).

Summary

1. Boron or silicon fluoride dissolved in an alcohol forms with mercuric oxide a catalyst for acetylene reactions much superior to sulfuric acid.

2. Fluoboric and fluosilicic acids are probably the active constituents of these solutions, which have high electrical conductance and strong acid properties (Fig. 1).

3. Boron fluoride dissolved in ether to form $BF_3(C_2H_5)_2O$, b. p. 123° may also be used as a catalytic agent.

4. The catalysts are effective in very small quantities.

5. Using these catalysts, ethylidene ethers have been prepared from glycols, hydroxy acids and their derivatives by the acetylene method.

6. A number of these compounds have not previously been prepared and could not be made by any known methods from acetylene or from acetaldehyde.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A STUDY OF THE DEHYDRATION OF DERIVATIVES OF ORTHO-BENZOYLBENZOIC ACID

BY GREGG DOUGHERTY AND A. H. GLEASON

RECEIVED MAY 18, 1929 PUBLISHED MARCH 6, 1930

In a previous paper[1] it was stated that various methods for dehydrating o-benzoylbenzoic acid had been tried and that concentrated sulfuric acid appeared to be almost a specific for the conversion of this acid to anthraquinone. Velocity measurements gave a good constant at a variety of temperatures when values were substituted in the equation for a monomolecular reaction and the constancy was unaffected when the ratio of molecular concentrations was reduced to 13:1 (6:1 by weight), the lowest practical ratio.

The purpose of this work has been to compare the ease of formation of substituted anthraquinones from the corresponding substituted *o*-benzoylbenzoic acids. The method of carrying out the condensation was exactly the same as in the case of the unsubstituted acid, namely, equimolecular amounts of the reactants were dissolved in equal weights of concentrated sulfuric acid and the solutions were heated in a constant-temperature bath for a definite length of time.

Although a great variety of substituted o-benzoylbenzoic acids may be made by the Friedel–Crafts reaction, it was found that by no means all of them could be made to yield the corresponding anthraquinone, at least by the method which we used. In some cases traces of the anthraquinones were found but the yields were so small and the reaction product so com-

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[1] Dougherty and Gleason, THIS JOURNAL, 51, 310 (1929).

plex that analysis was impossible. Some of the compounds giving unsatisfactory results for one reason or another were as follows: 2'-hydroxy-4'-methylbenzoylbenzoic acid (m. p. 211°), mesityloylbenzoic acid (m. p. 212°), benzoylbenzamide (m. p. 162°), 4'-ethylbenzoylbenzoic acid (m. p. 126°), the propyl and butyl esters of o-benzoylbenzoic acid and benzophenone-*o,p'*-dicarboxylic acid (m. p. 235°). In the first two cases sulfonation of the acid occurred and there was no ring closure; in the third case there was no sulfonation but again no anthraquinone was formed; with the next three, small amounts of the anthraquinone were formed but the reaction product was a tarry mass and could not be worked. In the last case the anthraquinone was formed but the amount could not be determined by our method. Anthraquinones were obtained from neither o-benzoylbenzamide nor o-mesityloylbenzoic acid, although the condensation proceeds smoothly with *o*-benzoylbenzoyl chloride and with methyl o-benzoylbenzoate. The compounds giving the best results were the halogen and simple alkyl (methyl) derivatives. A list of these, with the percentage of the theoretical yield of the anthraquinone obtained, is given. The nomenclature used was based on the usual scheme of numbering the carbons in o-benzoylbenzoic acid.

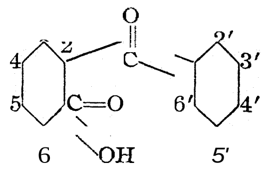

TABLE I

RESULTS OF EXPERIMENTS

		Percentage of anthraquinone formed in hours					M. p. of product, °C.
No.	Benzoylbenzoic acid	3 at 75°	4 at 75°	3 at 95°	4 at 95°	4 at 105°	
	2-	53.7	61.6				284
1	4'-Chloro-2-			7.76	10.4		210
2	4'-Bromo-2-			9.3	11.8		205
3	4'-Methyl-2-	31.5	38.5				177
4	6(3)-Chloro-2-			46.6	59.0		162
5	2'-5'-Dichloro-2-					25.0	187.5
6	3,6-Dichloro-2-			21.0	27.0		187.5
7	3',4'-Dimethyl-2-	100	100				183
8	2',4'-Dimethyl-2-	78.2	83.7				161
9	2'(5')-Methyl-5'(2')-chloro-2-	82.8	85.0				164

It will be noted in a general way that the halogen has a retarding influence on ring closure (Nos. 1, 2, 4, 5 and 6); this is marked when the halogen is on either benzene ring and increases with the number of halogens present; the retarding influence is greatest when the halogen is on the ring which does not contain the carboxyl group. Bromine seems to have a slightly smaller effect than chlorine (Nos. 1 and 2) but the difference is so slight and so close to the limits of experimental error that no certain conclusions can be drawn.

The influence of the methyl group is not so consistent as in the case of the halogen. One methyl group in Position 4′, the only monomethyl compound which we could obtain easily, had a decidedly depressing effect on the ease of anthraquinone formation. When more than one methyl group was present, however, the reactivity was increased considerably above that of the unsubstituted o-benzoylbenzoic acid (Nos. 7 and 8). Of these two, No. 7, in which one of the methyl groups is para to the hydrogen atom which is eliminated in the reaction, shows the greater reactivity. This would be expected according to the general rules which govern substitution in the benzene ring. It might also be expected for the same reason that the chlorine atom in No. 1 and the methyl group in No. 3 would retard rather than accelerate anthraquinone formation. However, in such a complicated system as o-benzoylbenzoic acid, not much stress may be placed on the directing influence of groups obtaining in simple substitution reactions. For example, in No. 8 both methyl groups are meta to the hydrogen atom and yet this compound is more reactive than either No. 1, No. 2 or the unsubstituted o-benzoylbenzoic acid. By comparing No. 5 and No. 9, it can be seen that the retarding effect of chlorine is more than equaled by the accelerating effect of methyl when the two substituents are in the ring.

Mechanism of the Reaction.—When reaction velocity measurements were made using various substituted o-benzoylbenzoic acids, in no case was a constant for a momomolecular reaction obtained over any considerable period of the reaction time. The proposed mechanism in the case of the unsubstituted acid[1] involved a rapid reaction between o-benzoylbenzoie acid and sulfuric acid in which water was eliminated, and a much slower decomposition of the resulting compound, which was the step in the process actually measured. It would be quite apparent that if the two steps, in the case of the substituted acids, became of the same order of magnitude as regards velocity, it might be difficult to express the rate of the reaction in terms of any simple velocity equation. The water in this case would be eliminated at a measurable rate instead of very rapidly and there would be a progressive diminishing of the condensing power of the sulfuric acid. It seems probable that the failure to get results with the substituted acids comparable to those obtained when the unsubstituted compound was used may be accounted for in this way.

Experimental

The experimental procedure was much the same as that outlined in Part I,[1] with the single exception that it was frequently found necessary to dissolve the uncondensed benzoylbenzoic acids with dilute sodium carbonate, due to the fact that the sodium salts of the acids appeared to be much less soluble in the excess alkalinity of sodium hydroxide.

All of the substituted benzoylbenzoic acids were made by the Friedel–

Crafts synthesis using either the substituted phthalic anhydride and benzene or a substituted benzene and the anhydride. The resulting acids were recrystallized from various solvents until a high degree of purity was reached, *i. e.*, until the melting point agreed with that found in the literature, or until a sharp melting point was obtained in case it could not be found in the literature (Nos. 4 and 8). No serious difficulties were encountered due to the simultaneous formation of isomers.

Acids 1, 2 and 3 (m. p. 147.5, 172 and 140°, respectively) were prepared from phthalic anhydride and the monosubstituted benzene. No. 4 (m. p. 233.5') was made from 3-chlorophthalic anhydride and benzene, the anhydride being prepared from the 3-nitro derivative as described by Bogert and Boroschek.[2] This compound could not be found in the literature so an analysis was made for chlorine: calcd., 13.62; found, 13.25. The high melting point of this acid seemed to indicate that it was the 6-chloro-2-benzoylbenzoic acid if analogy may be drawn from the fact that the 3-nitro-2-benzoylbenzoic acid has a melting point of 157–160° and the 6-nitro compound a melting point of 220–221°.[3] No. 5 (m. p. 169") was prepared according to the method of Phillips,[4] although the yields were considerably below 27% of the theoretical which he obtained. No. 6 (m. p. 168.5') was prepared from 3,6-dichlorophthalic anhydride and benzene; Nos. 7 and 8 (m. p. 161.5 and 143°) from phthalic anhydride and o- and m-xylene, respectively. No. 9 (m. p. 165") was prepared from phthalic anhydride and #-chlorotoluene. Benzophenone-*o,p'*-dicarboxylic acid was made by oxidizing No. 3 with alkaline permanganate.[5] The melting points of the product of each reaction are listed in the last column of the table and agree very closely with those given in the literature.

Summary

A number of substitution products of o-benzoylbenzoic acid have been synthesized, and attempts have been made to convert these into the corresponding anthraquinones. It was found that complete conversion took place in the case of the monohalogen and simple alkyl derivatives. A comparison was then made between the ease of ring closure of these derivatives and that of the unsubstituted acid.

Velocity measurements and constants indicated a fundamental difference between the mechanism of conversion of these acids and the unsubstituted acid, for which an explanation was offered.

A new compound, 6(3)-chloro-2-benzoylbenzoic acid, was prepared; melting point, 233.5°.

PRINCETON, NEW JERSEY

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[2] Bogert and Boroschek, THIS JOURNAL, 23,751 (1901).

[3] Lawrence, *ibid.*, 42, 1871 (1920).

[4] Phillips, *ibid.*, 48, 3198 (1926).

[5] Limpricht, *Ann.*, 309, 98 (1899).

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

THE CONSTITUTION OF SALTS OF CERTAIN CYCLIC IMIDES

BY THEODORE W. EVANS AND WILLIAM M. DEHN

RECEIVED JULY 1, 1929 PUBLISHED MARCH 6, 1930

Following the suggestion of Teuchert[1] the numerous salts of succinimide, phthalimide and saccharin have usually been given nitrogen–metal linkages. The chief support for these structures is afforded by reactions of some of these salts with alkyl halides which give the same products as are formed by treatment of the anhydrides with the respective alkyl bases

$$(CH_2CO)_2N\boxed{M + I}R \text{ and } (CH_2CO)_2\boxed{O + H_2}NR$$

However, with alkyl halides the silver and alkali metal salt differ in reaction, as do like salts of hydrocyanic acid, formanilide, diazo compounds, etc. With the same salt two reactions are sometimes simultaneously involved; the problem also is complicated by the apparent existence of two silver salts of phthalimide.

Therefore, placing the metal on nitrogen is hardly justified by the facts; the alternate form is the more probable, other evidence for which follows. When choice of union between an O or N atom exists, the metal usually, or more probably, assumes the former position. Direct substitution of M by R is not the only conceivable mechanism of reaction and is, indeed, the less probable one. When the imino hydrogen of cyclic imides is substituted by phenyl, etc., these derivatives themselves are still capable of forming salts. When the cyclic imides are treated with sodium in petroleum ether, toluene, etc., little or no hydrogen is evolved; apparently imino hydrogen does not condition the formation of these salts. The cyclic imides and the substituted cyclic imides form the same number of salts, which is always equal in number to the oxygen atoms present. For example, phthalimide and phthalanil both form mono- and di-metal salts, and saccharine forms mono-, di- and tri-metal salts. The initial compounds formed by the action of potassium or sodium hydroxide on unsubstituted cyclic imides are always additive compounds, which can be interpreted as hydrated salts. Therefore, the capacity for salt formation seems not dependent on the imino hydrogen but rather upon the carbonyl and sulfonyl groups.

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[1] Teuchert, *Ann.*, 134, 150 (1865). See also Laurent and Gerhardt, *Ann. chim. phys.*, [3] 24, 179 (1849); Dessaignes, *Ann.*, 82, 231 (1852); Menschutkin, *ibid.*, 162, 166 (1872); Landsberg, *ibid.*, 215, 200 (1882); Ley and Werner, *Ber.*, 39, 2179 (1906); Tschugaeff, *ibid.*, 40, 1973 (1907); Lyons, THIS JOURNAL, 47, 830 (1925); Cohn, *Ann*, 205, 301 (1880); Freudenburg and Uthemann, *Ber.*, 52, 1509 (1919); Remsen, Am. *Chem.* J., 6, 260 (1884–1885); Noyes, *ibid.*, 8, 180 (1896); Fahlberg and List, *Ber.*, 20, 1597 (1887); Fahlberg and Remsen, *Am. Chem.* J., 1, 431 (1879); Defournel, Bull. *soc. chim.*, 25, 322 (1876); Remsen and Palmer, *Am. Chem.* J., 8, 224 (1886).

Experimental Part

The salts were prepared by gently shaking bottles containing the solvent, the imide and the solid alkali, until the lump of alkali gave way to a powdery mass. The solvents used were alcohol, acetonitrile, methyl ethyl ketone and ether, Ether dried over sodium gave the best results. Equivalents of the imide and the alkali were used and in cases when all of the latter did not react, it could be removed from the precipitate, provided that minute chipping of it did not result from too energetic shaking. The crystalline or powdery products were filtered, washed, dried and the metal was determined by the sulfate method.

TABLE OF SALTS

(A = $C_4H_5O_2N$ = succinimide; B = $C_{10}H_9O_2N$ = succinanil; C = $C_8H_5O_2N$ = phthalimide; D = $C_{14}H_9O_2N$ = phthalanil; E = $C_7H_5O_3NS$ = saccharine; F = $C_{15}H_9O_3N$ = benzoylphthalimide; G = $C_{10}H_7O_3N$ = acetylphthalimide; H = $C_{15}H_{11}O_4NS$ = o-tolylsulfonylphthalimide)

			Sodium, %		Potassium, %	
Composition	**Solvent used**	**Crystals, etc.**	**Calcd.**	**Found**	**Calcd.**	**Found**
A·2 NaOH	CH_3CN	Amorphous	25.67	25.79		
A·2 NaOH	Et_2O	Prisms	25.67	25.41		
B·NaOH	EtOH, Et_2O	Gel. ppt.	10.69	9.37		
B·KOH	MeCOEt	Needles			16.91	17.40
B·KOH	CH_3CN	Plates			16.91	17.48
B·2 NaOH	MeCOEt	Prisms	18.03	20.87		
B·2 NaOH	CH_3CN	Prisms	18.03	17.44		
B·2 KOH	CH_3CN				27.24	28.36
C·2 NaOH	CH_3CN		20.26	21.41		
C·2 KOH	MeCOEt	Needles			30.16	30.05
D·NaOH	CH_3CN		8.74	8.77		
D·KOH	EtOH, Et_2O	Gel. ppt.			14.00	14.49
D·KOH	CH_3CN	Silky needles			14.00	15.26
D·2 KOH	CH_3CN	Prisms			23.32	23.46
D·2 KOH	MeCOEt	Prisms			23.32	22.85
E·2 NaOH	CH_3CN	Small prisms	17.48	18.97		
E·2 KOH	MeCOEt	Prisms			26.48	25.53
E·3 NaOH	CH_3CN	Plates	22.76	23.19		
E·3KOH	MeCOEt	Thin hexagon plates			33.37	32.37
F·KOH	Et_2O	Needles			12.72	13.55
F·2 KOH	Et_2O	Needles			21.52	22.43
G·KOH	Et_2O	Prisms			15.95	16.06
H·2 KOH	Et_2O	Prisms			18.91	19.12

Summary

A number of poly-metal alkali salts of cyclic imides and anils were prepared; their capacity to form salts is numerically equal to the number of oxygen atoms present; the metal is probably held in –OM rather than in –N–M combinations.

SEATTLE, WASHINGTON

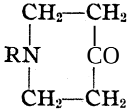
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

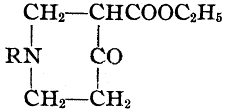
CATALYTIC REDUCTION OF 1-PHENYL- AND 1-BENZYL-4-PIPERIDONES[1]

BY N. W. BOLYARD

RECEIVED JULY 24, 1929 PUBLISHED MARCH 6, 1930

In an attempt to reduce the ketone group of 1-phenyl- and 1-benzyl-3-carbethoxy-4-piperidone, Thayer and McWvain[2] found that reduction of the aryl nucleus took place simultaneously and from the former compound 1-cyclohexyl-3-carbethoxy-4-piperidyl *p*-aminobenzoate hydrochloride was isolated but from the benzyl derivative no definite product could be obtained. Recently the preparation of a series of 1-alkyl-4-piperidyl benzoates was reported,[3] and it was pointed out that the catalytic reduction of the 1-alkyl-4-piperidones (I) took place much more readily than the reduction of the corresponding 3-carbethoxy-4-piperidones (II).


I


II

It, therefore, seemed desirable to prepare 1-phenyl- and 1-benzyl-4-piperidones and ascertain if possible their behavior on reduction.

These two piperidones were prepared from the corresponding 1-phenyl- and 1-benzyl-3-carbethoxy-4-piperidones[2] by identically the same procedure used in the preparation of the 1-alkyl-4-piperidones.[3] The hydrochlorides of the piperidones were subjected to catalytic reduction using Adams' platinum-oxide–platinum-black catalyst.

In the reduction of 1-phenyl-4-piperidone hydrochloride it was observed that if the reduction were stopped when enough hydrogen was absorbed to reduce the ketone group to a secondary alcohol, no definite crystalline product could be obtained after acylation with benzoyl chloride. If the reduction were allowed to proceed until no more hydrogen was absorbed, no difficulty was encountered in preparing a crystalline hydrochloride of the benzoate. The amount of hydrogen absorbed in this case was sufficient to form 1-cyclohexyl-4-hydroxypiperidine. In the reduction of I-benzyl-4-piperidone hydrochloride, the absorption of hydrogen stopped after a period of twelve hours and the amount absorbed was sufficient only to reduce the ketone group to a secondary alcohol.

The 1-cyclohexyl- and the 1-benzyl-4-hydroxypiperidines were not isolated as such but were acylated with benzoyl chloride and the resulting

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[1] This work was carried out at the suggestion of Professor S. M. McElvain of the Department of Organic Chemistry, University of Wisconsin.

[2] Thayer and McElvain, THIS JOURNAL, 49, 2862 (1927).

[3] Bolyard and McElvain, ibid., 51, 922 (1929).

benzoates crystallized as the hydrochlorides. In order to obtain additional information concerning local anesthetics of this type, these benzoates have been submitted for pharmacological study.

Experimental

1-Phenyl-4-piperidone Hydrochloride.—To 0.1 mole of 1-phenyl-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 ferric chloride solution by a drop of the reaction solution. The latter was then evaporated to dryness under diminished pressure and the tesidue was decomposed with concentrated sodium hydroxide. The free piperidone base was extracted with three 75-cc. portions of ether and the combined extract dried over anhydrous sodium sulfate for twenty-four hours. The hydrochloride was than precipitated with dry hydrogen chloride and recrystallized from an acetone–ether mixture. The yield was 78% of the theoretical of a product melting at 145–147°.

Anal. Calcd. for $C_{11}H_{14}NOCl$: Cl, 16.76. Found: Cl, 16.75, 16.76.

1-Benzyl-4-piperidone Hydrochloride.—This piperidone was prepared by exactly the same procedure used for 1-phenyl-4-piperidone hydrochloride. An 87% yield of the hydrochloride was obtained which melted at 159–161°.

Anal. Calcd. for $C_{12}H_{16}NOCl$: Cl, 15.71. Found: Cl, 15.57, 15.53.

Both of these piperidone hydrochlorides when crystallized from an alcohol–ether mixture gave chlorine analyses considerably lower than the calculated value, but when crystallized from an acetone-ether mixture the analyses checked with the calculated values. This behavior indicates that the hydrochlorides from the alcohol–ether solvent contained alcohol of crystallization. All attempts, however, to remove such alcohol by drying at atmospheric pressure or under diminished pressure were unsuccessful. The analyses were not changed by this treatment.

I-Cyclohexyl-4-piperidyl Benzoate Hydrochloride.—A solution of 3.5 *g.* of the 1-phenyl-4-piperidone hydrochloride in 40 cc. of 95% alcohol was shaken with 0.2 g. of Adams' platinum-oxide–platinum-black catalyst and hydrogen under a pressure of 2–3 atmospheres. After sixteen hours the theoretical amount of hydrogen had been absorbed to form 1-cyclohexyl-4-hydroxypiperidine hydrochloride. The catalyst was removed from the solution and the alcohol distilled under diminished pressure. To the residue which remained was added 7 cc. of benzoyl chloride and the mixture heated in an oil-bath at 130–140° for one hour. When the benzoylation had finished, 15 cc. of absolute alcohol was added to decompose the excess benzoyl chloride. The resulting alcohol solution was diluted with 150 cc. of ether and the precipitated 1-cyclohexyl-4-piperidyl benzoate hydrochloride allowed to crystallize. The product was recrystallized from an alcohol–ether mixture. A 57% yield of a product which melted at 250–252° was obtained.

Anal. Calcd. for $C_{18}H_{26}NO_2Cl$: Cl, 10.95. Found: Cl, 10.95, 11.00.

1-Benzyl-4-piperidyl Benzoate Hydrochloride.—This compound was prepared in exactly the same way as the 1-cyclohexyl-4-piperidyl benzoate hydrochloride. In this case, however, no more hydrogen than that required for the reduction of the ketone group was absorbed. After twelve hours the reduction had stopped. A 40% yield of the 1-benzyl-4-piperidyl benzoate hydrochloride was obtained. It melted at 198–200°.

Anal. Calcd. for $C_{19}H_{22}NO_2Cl$: Cl, 10.69. Found: Cl, 10.83, 10.92.

Pharmacological Report.—The 1-cyclohexyl and 1-benzyl-4-piperidyl benzoate hydrochlorides are being studied pharmacologically by Mr.

Charles L. Rose of the Lilly Research Laboratories, Indianapolis, Indiana. A preliminary report of this work is given in the following table.

PHARMACOLOGICAL DATA

1-Substituent	Average duration of anesthesia, minutes	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
Cyclohexyl	42	300	400	11	12.5	15	8
Benzyl	19	200	300	9	25	30	7

It will be seen from the table that 1-cyclohexyl-4-piperidyl benzoate hydrochloride has a lower subcutaneous and a higher intravenous toxicity than the 1-benzyl-4-piperidyl benzoate hydrochloride. Neither of these products shows any unusual anesthetic properties.

Summary

1. The preparation and properties of 1-phenyl- and 1-benzyl-4-piperidones have been described.

2. The catalytic reduction of these piperidones has been studied.

3. Two local anesthetics, 1-cyclohexyl and 1-benzyl-4-piperidyl benzoate hydrochlorides, have been prepared from the reduction products.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

THERMAL DATA ON ORGANIC COMPOUNDS. VI. THE HEAT CAPACITIES, ENTROPIES AND FREE ENERGIES OF SOME SATURATED, NON-BENZENOID HYDROCARBONS[1]

BY GEORGE S. PARKS,[2] HUGH M. HUFFMAN[3] AND S. BENSON THOMAS[4]

RECEIVED AUGUST 12, 1929 PUBLISHED MARCH 6, 1930

In five earlier papers[5] the entropies and free energies of nineteen compounds of carbon, hydrogen and oxygen were calculated from heat capacity data by means of the third law of thermodynamics. These results indicated that the entropy and free energy of an organic compound are related to its constitution in a simple additive manner. The present in-

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[1] This paper contains results obtained in an investigation of the heat capacities and free energies of some typical hydrocarbon compounds, listed as Project No. 29 of the American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by 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 No. 29.

[3] American Petroleum Institute Junior Research Associate.

[4] American Petroleum Institute Research Assistant (part time).

[5] Parks, THIS JOURNAL, **47**, 338 (1925); Parks and Kelley, *ibid.*, 47, 2094 (1925); Parks and Anderson, *ibid.*, 48, 1506 (1926); Parks and Huffman, *ibid.*, 48, 2788 (1926); Parks, Kelley and Huffman, *ibid.*, 51, 1800 (1929).

vestigation represents essentially a continuation of the past work and deals exclusively with compounds of carbon and hydrogen. This particular paper contains heat capacity data for the following fourteen saturated, non-benzenoid hydrocarbons: 2-methylbutane, n-hexane, n-heptane, 2-methylhexane, n-octane, 2,2,4-trimethylpentane, hexamethylethane, n-nonane, n-decane, di-iso-amyl, eicosane, pentacosane, tritriacontane and cyclohexane. In so far as it has been possible, we have utilized these data to calculate, by the third law of thermodynamics, the corresponding entropies and free energies. The latter values are especially interesting in view of the recent paper by Francis[6] in the same field.

Materials

For our work we have found it rather difficult to obtain compounds of sufficient purity, especially in the case of aliphatic hydrocarbons. A material which would be satisfactory to the organic chemist for the study of reactions, or of properties characteristic of the liquid state, may contain a few per cent. of isomers, the presence of which produces very erratic results when the specific heats in the crystalline state and the heat of fusion are measured. For this reason we have come to place little reliance upon the density of the sample or even upon the narrowness of the distillation range. From our own experience we feel that the sharpness of the melting point is by far the best criterion of purity, as even small amounts of impurity ordinarily cause very marked premelting. The details as to the source and character of the fourteen hydrocarbons employed are given in the following paragraphs.

2-Methylbutane.—This was a very pure Kahlbaum chemical, b. p. 28.0°. The product of a careful fractional distillation gave an extremely sharp melting point at 112.6°K.

n-Hexane, n-Nonane and *n*-**Decane.**—These compounds were very carefully synthesized for us by Mr. R. E. Marker of Yonkers, N. Y. They gave distillation ranges of from 0.2 to 0.5° at the accepted boiling points. However, only the hexane sample proved entirely satisfactory in our measurements. The other two materials gave a very irregular curve for the specific heats in the crystalline phase and showed marked premelting, which phenomena we took as evidence that the samples probably contained appreciable amounts of the isomers of the normal compounds. In view of the increasing number of isomers as we proceed up the series of paraffin hydrocarbons, it is extremely difficult to synthesize really pure compounds containing more than eight carbon atoms. However, isomeric impurities cannot affect appreciably the accuracy of specific heat determinations for the liquid state and, therefore, we shall present our data for liquid n-nonane and n-decane.

n-Heptane, 2-Methylhexane, n-Octane, **2,2,4-Trimethylpentane** and **Hexamethylethane.**—These compounds were prepared in the Research Laboratory of the Ethyl Gasoline Corporation under the direction of Dr. Graham Edgar. The details of the preparation of the two heptanes and the 2,2,4-trimethylpentane have been given in other places.[7] All five hydrocarbons had been synthesized very carefully and showed

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[6] Francis, *Ind. Eng. Chem.*, 19, 277 (1928).

[7] Edgar, Calingaert and Marker, THIS JOURNAL, 51, 1483 (1929); Edgar, Ind. Eng. *Chem.*, 19, 146 (1927).

a narrow distillation range, usually less than 0.2". The melting point was fairly sharp in every case.

Di-iso-amyl.—This material was a Kahlbaum preparation, supposedly of high grade, showing a boiling range of 0.8". However, like the n-nonane and n-decane previously described, it did not give a satisfactory melting point and specific heat curve for the crystalline state. Nevertheless, we believe that our data for this compound in the liquid state are fairly reliable.

Eicosane, Pentacosane and **Tritriacontane.**—These were straight-chained hydrocarbons which had been carefully recovered from paraffin wax in the Research Laboratory of the Standard Oil Company of Indiana. Their properties as well as their preparation by fractional distillation and fractional crystallization have been fully described elsewhere.[8] Throughout our measurements these substances gave every indication of excellent purity. The melting points were 36.4° ($C_{20}H_{42}$), 53.3° ($C_{25}H_{52}$) and 71.1" ($C_{33}H_{68}$).

Cyclohexane.—This was an Eastman product, m. p. 4.5°. It was subjected to twelve fractional crystallizations. The resulting material gave a very sharp melting point at 6.2° and an extremely sharp transition point at 185.9°K. It was undoubtedly one of the purest hydrocarbons that we have studied.

Experimental Results

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the fusion data. The apparatus and details of experimental procedure have been fully described in the first paper of this series. In view of the accuracy of the various measurements involved, the error in the experimental values thereby obtained is probably less than 1%, except in so far as impurities in the various samples may cause premelting or otherwise influence the results.

The specific heats and the fusion data, expressed in terms of the 15° calorie and with all weights reduced to a vacuum basis, appear in Tables I and II. For comparison with these values the literature contains only very meager data. Mabery and Goldstein[9] have studied the heat capacities between 0 and 50° of a number of hydrocarbons, including n-hexane, n-heptane, n-octane, n-nonane, n-decane and isodecane. They used an ice calorimeter and worked on materials derived from petroleum. Their result for n-octane at 25° is 3% below our curve; for the other compounds their values deviate by from 1.2 to 4.0% from our curves. The heat of fusion of only one of these compounds has been previously measured; Padoa[10] obtained 5.87 cal. per g. for cyclohexane as against our value of 7.41 cal.

Hexamethylethane and cyclohexane were found to exist in two crystalline forms with fairly definite transition temperatures at 148.1 and 185.9°K., respectively, and the corresponding heats of transition were measured by the same procedure used in the fusion determinations. The data thus obtained are recorded in Table III. In this connection it is noteworthy

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[8] Buchler and Graves, Ind. Eng. *Chem.*, 19, 718 (1927).

[9] Mabery and Goldstein, *Am. Chem.* **J., 28,** 69 (1902).

[10] Padoa, *Atti. Accad. Lincei,* **[5] 28, 239** (1919).

that the heat of transition of cyclohexane is quite large, while its heat of fusion is extremely small.

TABLE I

SPECIFIC HEATS

2-METHYLBUTANE: Crystals

Temp., °K.	80.4	83.0	86.7	89.2	92.4	92.5	97.1	102.0
C_p per g.	0.217	0.222	0 230	0.236	0.244	0.243	0.260	0.279

Liquid

Temp., °K.	120.5	125.3	140.3	169.5	186.1	200.6	215.8
C_p per g.	0.409	0.413	0.421	0.437	0.447	0.458	0.468
Temp., °K.	230.5	245.3	260.5	275.0	275.2	275.7	275.8
C_p per g.	0.480	0.492	0.507	0.519	0.518	0.519	0.521

n-HEXANE: Crystals

Temp., °K.	89.7	91.8	93.8	95.8	102.3	109.3
C_p per g.	0.218	0.221	0.223	0.226	0.236	0.247
Temp., °K.	115.0	122.7	129.7	135.3	141.1	153.9
C_p per g.	0.256	0.267	0.279	0.288	0.302	0.331

Liquid

Temp., °K.	183.6	187.4	217.4	237.0	255.5	275.0	288.5	295.1
C_p per g	0.468	0.471	0.480	0.487	0.502	0.516	0.527	0 531

n-HEPTANE: Crystals

Temp.. °K.	90.1	90.5	96.0	96.0	102.6	109.8
C_p per g.	0.205	0.206	0.216	0.215	0.226	0.236
Temp., °K.	122.2	128.5	134.6	140.5	145.3	150.9
C_p per g.	0.254	0.263	0.271	0.280	0.287	0.295

Liquid

Temp., °K.	188.0	200.0	217.4	235.8	240.4	258.0	262.5
C_p per g.	0.480	0.480	0.484	0.489	0.491	0.500	0.504
Temp.. °K.	275.4	276.0	279.5	287.5	291.3	294.2	299.2
C_p per g.	0.513	0.514	0.517	0.522	0.525	0.527	0.530

2-METHYLHEXANE: Crystals

Temp., °K.	85.9	87.6	89.8	92.5	94.1	101.4	107.4
C_p per g.	0.202	0.206	0.212	0.217	0.219	0.229	0.237
Temp., °K.	108.6	114.4	115.5	122.8	129.7	135.9	
C_p per g.	0.239	0.249	0.250	0.262	0.281	0.306	

Liquid

Temp., °K.	160.2	166.0	180.3	195.2	211.0	225.0
C_p per g.	0.427	0.430	0.439	0.449	0.460	0.469
Temp., °K.	240.3	255.4	275.8	280.6	286.2	292.4
C_p per g.	0.480	0.491	0.507	0.517	0.519	0.523

n-OCTANE: Crystals

Temp.. °K.	85.5	90.8	96.9	103.0	109.5	122.2	128.4	134.8
C_p per g.	0.188	0.196	0.209	0.219	0.227	0.244	0.252	0.258
Temp., °K.	146.6	152.7	161.2	171.6	176.9	181.6	180.4	195.9
C_p per g.	0.274	0.282	0.292	0.308	0.317	0.320	0.338	0.372

TABLE I (Continued)

Liquid

Temp., °K.	223.0	232.7	244.8	255.7	275.3	279.3	284.8	293.7
C_p per g.	0.482	0.483	0.487	0.493	0.504	0.508	0.513	0.518

2,2,4-TRIMETHYLPENTANE: **Crystals**

Temp., °K.	87.9	91.9	98.2	105.5	113.2	123.2
C_p per g.	0.181	0.190	0.201	0.217	0.232	0.250
Temp., °K.	129.4	135.2	140.9	147.7	152.8	
C_p per g.	0.260	0.271	0.285	0.303	0.325	

Liquid

Temp., °K.	169.6	173.4	177.8	188.3	194.4	213.8	218.5	230.2
C_p per g.	0.388	0.390	0.393	0.399	0.403	0.420	0.422	0.432
Temp., °K.	255.2	275.0	278.4	283.1	287.6	292.0	295.2	
C_p per g.	0.452	0.471	0.475	0.477	0.482	0.487	0.489	

HEXAMETHYLETHANE: **Crystals I**

Temp., °K.	88.8	92.4	98.3	105.8	113.5	122.7	129.8	136.4
C_p per g.	0.166	0.172	0.183	0.198	0.213	0.234	0.255	0.279

Crystals II

Temp., °K.	161.3	173.0	178.8	188.4	194.3	204.4	209.5	223.8
C_p per g.	0.308	0.326	0.332	0.345	0.353	0.369	0.374	0.394
Temp., °K.	229.1	242.5	250.5	259.7	275.5	281.0	291.2	295.4
C_p per g.	0.400	0.417	0.427	0.438	0.458	0.466	0.481	0.486

n-NONANE: **Liquid**

Temp., °K.	224.5	251.3	2553	2764	284.8	290.0	293.9	299.1
C_p per g.	0.484	0.492	0.493	0.506	0.512	0.517	0.521	0.524

n-DECANE: **Liquid**

Temp., °K.	242.3	254.9	275.1	277.6	287.7	295.5
C_p per g.	0.483	0.487	0.503	0.506	0.514	0.520

DI-ISO-AMYL: **Liquid**

Temp., °K.	223.2	227.5	244.5	275.0	278.2	283.3	289.4	295.0
C_p per g.	0.453	0.455	0.467	0.492	0.493	0.498	0.501	0.507

n-EICOSANE: Crystals

Temp., °K.	93.6	99.1	123.9	143.3	163.0	179.0	195.4
C_p per g.	0.175	0.182	0.212	0.234	0 258	0.276	0.298
Temp., °K.	210.1	224.5	236.5	250.5	262.7	279.1	
C_p per g.	0.319	0.340	0.360	0.389	0.414	0.512	

n-PENTACOSANE: Crystals

Temp., °K.	91.3	97.8	122.7	152.0	180.3	194.5	199.9
C_p per g.	0.168	0.176	0.205	0.237	0273	0.292	0.300
Temp., °K.	223.5	240.7	256.9	275.1	279.4	284.4	294.5
C_p per g.	0.334	0.361	0.391	0.430	0.446	0.467	0.521

n-TRITRIACONTANE: Crystals

Temp., °K.	93.7	1222	146.0	163.3	165.0	184.2
C_p per g.	0.168	0.201	0.227	0.248	0.249	0.272
Temp., °K.	207.0	227.3	252.0	275.3	281.1	294.4
C_p per g.	0.303	0.331	0.368	0.412	0.426	0.463

TABLE I (Concluded)

CYCLOHEXANE: Crystals I

Temp., °K.	91.8	97.6	105.1	112.8	126.6	132.1	137.7
C_p per g.	0.157	0.164	0.173	0.181	0.196	0.203	0.209
Temp., °K.	144.1	150.0	162.9	166.0	168.4	177.5	
C_p per g	0.216	0.223	0.239	0.245	0.247	0.263	

Crystals II

Temp., °K.	209.0	214.1	223.7	229.0	234.8	239.9	244.8	265.6
C_p per g.	0.316	0.320	0.325	0.329	0.334	0.337	0.342	0.362

Liquid

Temp., °K.	283.1	285.3	286.6	290.7	298.9
C_p per g.	0.422	0.423	0.425	0430	0.440

TABLE II

FUSION DATA[a]

Substance	M. p., °K.	Heat of fusion (cal. per g.) 1st result	2nd result	Mean
2-Methylbutane	112.6	16.96	16.92	16.94
n-Hexane	178.6	34.88	34.90	34.89
n-Heptane	182.2	33.84	33.73	33.78
2-Methylhexane	154.0	21.17	21.16	21.16
n-Octane	215.6	41.90	42.17	42.04
2,2,4-Trimethylpentane	165.3	18.89	18.95	18.92
Eicosane	309.7	52.0	...	52.0
Cyclohexane	279.3	7.39	7.43	7.41

[a] In the calculation of these fusion values the marked rise in the specific heat of the solid as the melting point is approached was attributed to premelting, and the heat absorbed in this region in excess of that obtained by extrapolation of the specific-heat data at lower temperatures was added to the heat absorbed at the melting point.

TABLE III

TRANSITION DATA

Substance	Transition temperature	Heat of transition (cal. per g.) 1st result	2nd result	Mean
Hexamethylethane	148.1°K.	4.20	...	4.20
Cyclohexane	185.9°K.	19.07	19.07	19.07

Discussion

Entropies of the Compounds.—Using the data contained in Tables I, II and III in conjunction with the third law of thermodynamics, we have calculated the molal entropies at 298.1°K. for all the hydrocarbons except n-nonane, n-decane and di-iso-amyl. In these calculations we have employed the extrapolation method of Kelley, Parks and Huffman[11] for estimating the entropy increases for the crystals, Col. 2 of Table IV, from 0 to 90°K. The various entropy increments from 90 to 298.1°K., which appear in Cols. 3, 4 and 5 of the table, were obtained by the usual methods directly from the experimental data. The results for the total entropy in calories per degree appear under the heading "S_{298} experimental" in

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[11] Kelley, Parks and Huffman, *J. Phys. Chem.*, *33*, 1802 (1929).

the sixth column. In the case of the four hydrocarbons which are normally crystalline at 298°K. and 1 atm. pressure, we have also calculated the entropy of fusion at 298° so as to obtain a value for the entropy of each liquid, even though the liquid state may be unstable at this temperature. For this calculation of the entropy of fusion we have employed unpublished data, obtained by Parks and Todd, for the specific heats and heat of fusion of hexamethylethane, pentacosane and tritriacontane.

In the previous studies an entropy increase of 7.8 E. U. per CH_2 increment was found for the normal alcohol series and of 8.0 E. U. for the normal aliphatic acid series, when all the compounds involved were in the liquid state. In the present case we have found an average increase of 7.7 units per CH_2 increment for the normal liquid hydrocarbons. In other words, the entropy of a normal hydrocarbon in the liquid state at 298°K. can be calculated by the equation, $S_{298} = 25.0 + 7.7\ n$, where n is the number of carbon atoms in the straight chain. By this method the values of "S_{298} predicted" in the last column of Table IV were obtained for n-hexane, n-heptane, n-octane, eicosane, pentacosane and tritriacontane, all in the liquid state. They are in excellent agreement with the experimental results.

TABLE IV

ENTROPIES OF THE HYDROCARBONS PER MOLE

Substance	Crystals 0–90°K	Crystals Above 90°K.	Fusion	Liquid	S_{298} experimental	S_{298} predicted
2-Methylbutane	13.74	4.28	10.84	31.90	60.8	59.0
n-Hexane	15.64	16.70	16.84	21.90	71.1	71.2
n-Heptane	16.97	18.80	18.58	24.51	78.9	78.9
2-Methylhexane	16.74	13.81	13.75	30.86	75.2	74.4
n-Octane	18.45	26.93	22.27	1833	86.0	866
2,2,4-Trimethylpentane	15.90	17.30	13.06	28.90	75.2	73.1
Hexamethylethane (solid)	15.46	45.97[a]			61.4	
Hexamethylethane (liquid)	15.46	45.97[a]	4.0		65.4	68.6
Eicosane (solid)	40.50	93.00	..		133 5	...
Eicosane (liquid)	40.50	93.00	47.0		180.5	179.0
Pentacosane (solid)	49.2	111.2			160.4	..
Pentacosane (liquid)	49 2	111.2	56 6		217.0	217 5
Tritriacontane (solid)	63 8	146.0			209 8	..
Tritriacontane (liquid)	63.8	146.0	70.3	. .	280.1	279.1
Cyclohexane	12.08	32.53[a]	2.23	2.35	49.2	.

[a] This value includes the entropy increase for both crystalline forms as well as the entropy effect for the transition between them.

Compared with the normal compound, isomers with branches on the chain have a lower entropy, which depends upon the amount of the branching. From the study of a number of branched compounds, both hydrocarbons and alcohols, we have found an average decrease of 4.5 E. U. on substituting" a CH_3 branch for a CH_2 group in the chain. Thus the entropy of a branched hydrocarbon in the liquid state is given by the equation, $S_{298} = 25.0 + 7.7\,n - 4.5\,r$, where n is the total number of carbon atoms in the molecule and r represents the number of methyl branches on the straight chain. In this way we have obtained the predicted values for 2-methylbutane, 2-methylhexane, 2,2,4-trimethylpentane and liquid hexamethylethane. On the whole these values agree fairly well with the experimental results.

Thus we are justified in concluding that S_{298} for any aliphatic saturated hydrocarbon in the liquid state can be predicted to within a few per cent. from the constitutional formula of the substance.

The experimentally determined entropy of cyclohexane (49.2 E. U.) is much smaller than that of n-hexane; and, in general, it seems certain that the entropy effect of a carbon ring is much less than that of the same number of atoms in a straight chain. However, at present we do not possess any means of predicting the entropies of such ring compounds.

The Free Energies of Nine Hydrocarbons.—To the chemist the free energy of formation of a compound is of greater interest than its entropy. Accordingly we have also calculated the free energies of nine of these hydrocarbons by means of the third law of thermodynamics and the fundamental thermodynamic equation, $\Delta F = \Delta H - T\Delta S$.

The essential data are given in Table V. For obtaining the figures for the ΔH of formation of eight of the compounds we have used the heats of combustion given in the "International Critical Tables,"[12] converted to 25° for our present purpose. The heat of combustion of pentacosane was computed from the result of Richards and Davis[13] for "hard paraffin." The literature contains no reliable values for $C_{20}H_{42}$ and $C_{33}H_{68}$. The ΔH_{298} values were then calculated from these data by use of 68,330 cal.,[14] and 94,270 cal.[15] for the heats of combustion of hydrogen and graphite carbon, respectively. Column 4 contains the entropy of formation of each compound, which is simply the difference between its S_{298} and the corresponding values for the entropies of the elements contained therein. For this purpose the respective entropies of carbon and hydrogen were taken as 1.3[16] and 14.8[17] E. U. per gram atom.

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[12] "International Critical Tables," Vol. V, p. 163.

[13] Richards and Davis, THIS JOURNAL, 39, 352 (1917).

[14] The value in the "International Critical Tables," Vol. V, p. 176, is 286.2 kj. at 18°; this is equivalent to 68,330 cal. at 25°.

[15] Roth and Naeser, *Z. Elektrochem.*, 31, 461 (1925).

[16] Lewis and Gibson, THIS JOURNAL, 39, 2581 (1917).

[17] Giauque and Wiebe, *ibid.*, *50*, 121 (1928). In a recent paper Giauque and Johnston [*ibid.*, *50*, 3221 (1928)] consider that this value for the entropy of hydrogen should be increased by 2.2 E. U. per gram atom at 298.1°K. However, their new value is larger than any result obtained experimentally, either by a direct or indirect application of the third law of thermodynamics, and they now believe that only 0.8 E. U. of his increase need be considered for chemical reactions (Johnston, personal communi-

The molal free energies appear in the last column of the table. The results for hexamethylethane and pentacosane refer to the solid state. According to our estimate, based upon the unpublished data of Parks and Todd, the free energies of the corresponding liquids at 298°K. will be algebraically greater than these results by about 300 cal. and 1600 cal., respectively. For comparative purposes the accuracy of the free energy data is largely limited by the accuracy of the combustion data employed. In the case of the two heptanes and three octanes these combustion values were obtained recently by the U. S. Bureau of Standards and are probably accurate to about a thousand calories. For the other four compounds the errors may easily be twice this figure.

TABLE V

THERMAL DATA AT 298.1°K.

The 15° cal. is used throughout and all weights have been reduced to a vacuum basis

Substance	*Heat of combustion at constant pressure*	ΔH_{298}, *cal.*	ΔS_{298}, *E. U.*	ΔF°_{298}, cal.
2-Methylbutane	838,000	-43,300	-123.3	-6,600
n-Hexane	990,200	-53,300	-143.9	-10,800
n-Heptane	1,149,400	-57,100	-167.0	-7,300
2-Methylhexane	1,148,400	-58,100	-170.7	-7,200
n-Octane	1,304,500	-64,600	-190.8	-7,700
2,2,4-Trimethylpentane	1,303,400	-65,700	-201.6	-5,600
Hexamethylethane (s)	1,301,300	-67,800	-215.4	-3,600
Pentocosane (s)	3,941,500	-191,800	-641.7	- 500
Cyclohexane	938,700	-36,900	-136.2	+3,700

Even in view of these uncertainties the data serve to bring out two important points. First, there is evidence of a small but definite increase in molal free energy as we proceed up the series of normal paraffins. Thus between n-hexane and liquid pentacosane there is a free energy increase of 11,900 cal. or about 630 cal.[18] per CH_2 increment. This trend, being small, is easily masked over the range of a few CH_2 increments by experimental errors in the combustion values and, in fact, was overlooked by one[5] of us in an earlier study of the simpler normal alcohols. That it actually exists, however, can be demonstrated in another way. From studies on various series of normal aliphatic compounds, it has been demonstrated that a fairly definite increase of about 156,300 cal.[19] occurs in the heat of combustion per CH_2 increment. This means that the ΔH_{298} of formation must decrease by 6300 cal. per CH_2 group. On the other hand, we find

cation). Until the question has been investigated further, we shall use 14.8 E. U., as in preceding papers.

[18] Of course, it should be noted that if the entropy of hydrogen be increased by 0.8 E. U. per gram atom, as suggested in Ref. 17, this free energy increase per ΔCH_2 will become about 1100 cal.

[19] Kharasch and Sher, *J. Phys. Chem.*, 29, 629 (1925); see also Verkade and Coops, *Rec. trav. chim.*, 46, 911 (1927), and Verkade, Coops and Hartman, *ibid.*, 45, 585 (1926).

that the TAS term decreases by 6900 cal. and consequently ΔF°_{298} must increase by approximately 600 cal.

The data also indicate that the free energy of a branched isomer is probably somewhat higher than the value for the normal hydrocarbon and that the more extensive the branching, the larger becomes this difference. In other words, the branched isomers are thermodynamically unstable with reference to the normal compound. This point is now being more thoroughly investigated in our laboratory in a study of the free energies of the nine isomeric heptanes recently prepared by Edgar and co-workers.

It should be noted that cyclohexane has a free energy value about 14,000 cal. above that of normal hexane. Evidently the withdrawal of a mole of hydrogen and the formation of a ring are accompanied by a very appreciable free energy increase.

Before concluding, the authors wish to thank the Research Laboratory of the Ethyl Gasoline Corporation and the Standard Oil Company of Indiana for the loan of valuable hydrocarbon samples.

Summary

1. The specific heats of fourteen saturated, non-benzenoid hydrocarbons have been measured over a wide range of temperatures.

2. The heats of fusion of eight of these compounds have also been determined. In the cases of hexamethylethane and cyclohexane, which exist in two crystalline forms at low temperatures, the heat of transition has been measured.

3. The entropies of eleven of the compounds have been calculated from these heat capacity data. Two empirical equations for the estimation of the entropies of aliphatic hydrocarbons have been tested with the results.

4. The free energies of nine of these hydrocarbons have also been calculated. Apparently there is a small free energy increase, about 600 cal., per CH_2 increment in the normal hydrocarbons. In isomeric hydrocarbons the free energy level becomes higher with increased branching.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 227]

THE ACTION OF SODIUM ON BETA-CHLROO-ALPHA,ALPHA, ALPHA-TRIPHENYLETHANE IN LIQUID AMMONIA. REARRANGEMENT OF AN ORGANO-ALKALI COMPOUND

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When this investigation was undertaken no colored organo-alkali compounds had been reported except those in which one or more aromatic rings were attached to the same carbon atom as was the alkali metal.[3] A formula containing a quinonoid ring may be readily constructed for these compounds and the existence of tautomers so constituted had been suggested as the source of their color.' It appeared to be of interest, therefore, to investigate the influence upon the properties of the carbon–hydrogen **and** carbon–sodium bonds, in hydrocarbons and organo-alkali compounds, when aromatic rings are present only in the β-position with respect to the carbon atom in question. If organo-alkali compounds of this type were colored, the hypothesis just mentioned would require the assumption of a tautomeric quinonoid structure containing a trimethylene ring.

It has been shown that α,α,α-triphenylethane does not react with potassium amide in liquid ammonia,[5] and attempts to prepare a nonaphenyl-*tert.*-butane were unsuccessful. However, since it had been observed[B] that sodium benzylide could be prepared from sodium and benzyl bromide in liquid ammonia, although potassium amide is also without action on toluene, it was suspected that an organo-alkali compound might be obtained when β-chloro-α,α,α-triphenylethane was treated with sodium. This proved to be correct but when the red compound which resulted was decomposed with ammonium chloride (which replaces the alkali metal with hydrogen) the product was α,α,β-triphenylethane. It is obvious that a rearrangement occurred[6] and a preliminary study which has been made of this rearrangement is the subject of this paper.

[1] National Research Fellow.

[2] A portion of this material was submitted by N. W. Mitchell in a thesis for the degree of Bachelor of Science at the Massachusetts Institute of Technology.

[3] More recently, the preparation of colored alkali metal derivatives of purely aliphatic hydrocarbons has been described [Salzberg and Marvel, THIS JOURNAL, 50, 1737 (1928); Schlenk and Bergmann, *Ann.*, **463**, 2–97 (1928)].

[4] (a) Gomberg, *Ber.*, 40, 1875 (1907); (b) Schmidlin, "Das Triphenylmethyl," Stuttgart, 1914, p. 205; (c) Blicke, THIS JOURNAL, 46, 2560 (1924); 47, 229 (1925).

[5] Wooster and Mitchell, ibid., 52, 688 (1930).

[6] It has been shown recently by Ziegler and Crossmann [Ber., 62, 1768 (1929)] that the reaction between sodium and 1,1,3-triphenylindene, reported by Schlenk and Bergmann [*Ann.*, 463, 125 (1928)], involves a similar rearrangement. The experiments which demonstrated the rearrangement of sodium triphenylethide were completed before the publication of Schlenk and Bergmann's paper.

Experimental Part

Apparatus and Materials.—The apparatus employed in the experiments with liquid ammonia solutions has been described in previous communications.[5,7]

The method of preparing the two triphenylethanes has also been given.[5] β-Chloro-α,α,α-triphenylethane was obtained by the method of Cone and Robinson,[8] and purified by crystallization from petroleum ether.

Attempted Preparation of Nonaphenyl-*tert.*-butane.—Three attempts to prepare this hydrocarbon directly by the interaction of potassium triphenylmethide and chloroform proved unsuccessful.

The chief product of the reaction, in addition to potassium chloride, was a yellow mass which did not crystallize upon cooling and could not be recrystallized from alcohol, benzene and other solvents. When distilled at 100–150° under 0.2-mm. pressure, a solid was obtained which, after purification by crystallization from alcohol, proved to be triphenylmethane. This result may have been due either to ammonolysis of the chloroform in liquid ammonia or to a decomposition of the reaction product in the course of vacuum distillation.

Another attempt was made involving the stepwise substitution of triphenylmethyl groups into methane. This was halted by the inactivity of β-chloro-α,α,α-triphenylethane, which would not react with potassium triphenylmethide in liquid ammonia.

The Action of Sodium on β-Chloro-α,α,α-Triphenylethane in Liquid Ammonia.—When this experiment was carried out in a small reaction tube in the usual manner, a red color was imparted to the solution and all the sodium ultimately reacted, even when large quantities of the metal were employed. Ammonium chloride decolorized the mixture rapidly but in several such experiments only a quantity of the unchanged chloride was recovered. In another of these experiments a very large excess of sodium was used and a liquid mixture was isolated from the reaction residue which solidified below 0°. It was partially frozen and pressed out between filter papers cooled between blocks of ice. Its melting point was raised in this manner to 47°, but at this point the quantity of material became too small for further manipulation.

Success was attained only when the procedure was modified so that the finely pulverized chloride was slowly "dusted" (in the course of about two hours) into a very concentrated solution of sodium contained in a large Dewar flask, the mixture being vigorously agitated by means of the combined action of a stream of gaseous ammonia and a rapidly rotating mechanical stirrer. The stirring was continued for four hours after all of the chloride had been introduced, fresh pieces of sodium being added from time to time. The action of ammonium chloride instantly decolorized the solution and a red precipitate was thrown down. The ammonia was allowed to evaporate completely and water added to the residue. The aqueous solution was filtered and the crystals remaining on the filter paper were crystallized once from alcohol. White needles were obtained which melted at 53.5–54.5°. The melting point remained unchanged upon further recrystallization and upon mixing this product with a sample of α,α,β-triphenylethane. The ultimate results of the reactions involved are probably those expressed in the following equations

$$(C_6H_5)_3C—CH_2Cl + 2Na \longrightarrow NaCl + C_{20}H_{17}Na \qquad (1)$$

$$C_{20}H_{17}Na + NH_4Cl \longrightarrow NaCl + NH_3 + (C_6H_5)_2CH—CH_2C_6H_5 \qquad (2)$$

The Structure of the Red Sodium Compound.—The product of the reaction with ammonium chloride shows that a rearrangement has taken

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[7] Wooster, THIS JOURNAL, 51, 1856 (1929).

[8] Cone and Robinson, Ber., 40,2164 (1907).

[9] The apparatus employed has been described by Kraus and Foster, THIS JOURNAL, 49, 460 (1927).

place, but it leaves the exact structure of the sodium compound in doubt, for it is impossible to tell which hydrogen atom in α,α,β-triphenylethane is the one which replaced the sodium atom. Accordingly, attempts were made to substitute some group other than hydrogen for the sodium atom and thus obtain a characteristic derivative. These attempts are reported below, but all were unsuccessful.

In a previous communication[5] the authors have shown that all the organo-alkali derivatives of phenylated methanes and ethanes which have been found to be stable in liquid ammonia apparently contain the grouping $(C_6H_5)_2C(M)$- (M = alkali metal). Since the sodium compound in question is stable in ammonia it probably contains this grouping. For this reason the constitution represented in the formula $(C_6H_5)_2C(Na)$-$CH_2C_6H_5$, may be accepted provisionally as its structure.

The Action of Carbon Dioxide on the Red Sodium Compound.—The only derivatives of such possible salts as $(C_6H_5)_2C(Na)CH_2C_6H_5$ and $(C_6H_5)_2CHCH(Na)C_6H_5$ which are known are the carboxylic acids, which might be expected to result from the action of carbon dioxide on these salts. Experiments showed that carbon dioxide could not be used in liquid ammonia solutions since ammonium carbamate was formed too rapidly.

In one experiment the residue after evaporation of the ammonia from a preparation of the sodium compound was treated with anhydrous ether but no solution was formed and the treatment with carbon dioxide under these conditions was also unsuccessful. It is not certain whether the salt is actually insoluble in ether or whether it was coated with a layer of the excess sodium. Unfortunately, the use of a large quantity of this metal is necessary, since its reaction with ammonia to form the amide is apparently catalyzed by some of the reacting materials or products.

Attempts to Prepare Reference Compounds.—The use of such reagents as methyl iodide, ethyl bromide, etc., is an obvious resort, but before such reactions could yield the desired information the expected derivatives must be synthesized independently for comparison with the actual reaction products. Attempts to obtain the corresponding halides from diphenylethylcarbinol and diphenylbenzylcarbinol for use in an independent synthesis of such reference compounds were also unsuccessful. Only the corresponding ethylene derivatives were obtained when the reagents were thionyl chloride or hydrogen chloride gas.

The sole preparation of these chlorides mentioned in Beilstein's "Handbuch" is that of Klages and Heilmann.[10] Since these investigators obtained liquids which they assumed to be the chlorides merely because the corresponding ethylene derivatives could be isolated after the liquids

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[10] Klages and Heilmann, Ber., 37, 1450, 1455 (1904).

were boiled with pyridine, it is somewhat doubtful whether they actually obtained such chlorides.[11]

The Mechanism of the Rearrangement.—Although, as has just been noted, the constitution of the red compound is still somewhat uncertain, some study has been devoted to the possible mechanism of the rearrangement. Since the action of ammonium chloride upon a liquid ammonia solution of an organo-alkali salt is that of simple hydrolysis by a strong acid, it is probable that the rearrangement occurred at an earlier stage in the process.

Furthermore, the structure of the original chloride seems to be in little doubt. Its properties agree with those described by Cone and Robinson[8] and are distinctly different from those of the isomeric α-chloro-α,α,β-triphenylethane as described by Klages and Heilmann.[10] It has just been stated that it is somewhat doubtful whether these investigators actually obtained this compound. However, the evidence indicates that such a chloride if it exists at all is very unstable and would differ markedly from the very stable one assumed to be β-chloro-α,α,α-triphenylethane. There is no reason to suspect that the halogen is in a phenyl nucleus and the reaction with sodium is not of the type to be expected of such a compound.[12] Finally, the presence of halogen in the ring would not account for the rearrangement observed. It is very likely, in consequence, that the rearrangement occurs during the reaction with sodium.

Two very different mechanisms may be suggested; I—that the normal sodium salt was first formed

$$(C_6H_5)_3C—CH_2Cl + 2Na \longrightarrow NaCl + (C_6H_5)_3C—CH_2Na \qquad (3)$$

and this then rearranged in some such manner as that indicated.

$$(C_6H_5)_3C—CH_2Na \longrightarrow (C_6H_5)_2C(Na)—CH_2C_6H_5 \qquad (4)$$

II. Another mechanism would assume an initial loss of hydrogen chloride

$$(C_6H_5)_3C—CH_2Cl \longrightarrow (C_6H_5)_3C—CH< + HCl \qquad (5)$$

$$(C_6H_5)_3C—CH< \longrightarrow (C_6H_5)_2C{=}CHC_6H_5 \qquad (6)$$

$$HCl + Na \longrightarrow NaCl + {}^1/_2\, H_2 \qquad (7)$$

$$(C_6H_5)_2C{=}CHC_6H_5 + 2Na \longrightarrow (C_6H_5)_2C(Na)—CH(Na)C_6H_5 \qquad (8)$$

$$(C_6H_5)_2C(Na)—CH(Na)C_6H_5 + NH_3 \longrightarrow (C_6H_5)_2C(Na)—CH_2C_6H_5 + NaNH_2 \qquad (9)$$

$$(C_6H_5)_3C—CH_2Cl + 3Na + NH_3 \longrightarrow {}^1/_2\, H_2 + NaCl + NaNH_2 + (C_6H_5)_2C(Na)—CH_2C_6H_5 \qquad (10)$$

The rearrangement itself is expressed by Equations 5 and 6 and is analogous to that observed upon heating β-chloro-α,α,α,β-tetraphenylethane or treating this halide with water, phenylmagnesium bromide or benzene

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[11] In this connection it is interesting to note that three attempts by one of us (N. W. M.) to obtain triphenylethylene by dehydration of diphenylbenzylcarbinol with acetic anhydride were all unsuccessful. This suggests that the dehydrations reported by us may have involved the intermediate formation of a very unstable chloride.

[12] White, THIS JOURNAL, 45, 779 (1923).

and aluminum chloride.[13] Similar equations have been suggested for other rearrangements involving "unilateral" abstraction of hydrogen halides by Tiffeneau, Stieglitz and others.[14] The remaining reactions are those expected as a consequence of the presence of sodium and ammonia.

That expressed in Equation 8 has been shown to take place by separate experiments employing sodium and also potassium. In the latter case, triphenylethylene[15] was treated with excess potassium and after reaction had occurred the color of the free metal was discharged by adding an iron oxide catalyst to convert the metal into its amide. This left a deep red solution and from the amount of hydrogen evolved in the process it was calculated that two atoms of potassium had reacted with the hydrocarbon. Ammonium chloride decomposed the salt and α,α,β-triphenylethane was obtained from the residue.

Reaction 9 is suggested as a result of the information reported in a previous communication[6] that only those potassium derivatives of phenylated methanes and ethanes which contain the $(C_6H_5)_2C(K)^-$ group resist ammonolysis in liquid ammonia. This suggestion is supported by the fact that the action of benzyl chloride upon the product of potassium and triphenylethylene yields the same substance that is produced when this halide is added to the reaction product of potassium amide and α,α,β-triphenylethane.[16]

Since the reaction

$$Na + NH_3 \longrightarrow NaNH_2 + {}^1/_2H_2 \qquad (11)$$

always occurred during the actual experiment, it is impossible to distinguish between the two alternative mechanisms by a study of the final products, for these are the same. This is evident when Equation 11 is added to 3 and 4, for the sum is identical with 10.

The Action of Sodium on β-Chloro-α,α,α-triphenylethane in Indifferent Solvents.—If the rearrangement could be carried out in the absence of ammonia or other reactive solvent, Reactions 9 and 11 could be eliminated and the final products predicted by the two mechanisms would differ. (The influence of employing an excess concentration of the halide instead of the metal might lead to a synthesis of the Wurtz–Fittig type but would not invalidate this statement.) Unfortunately, this test was defeated by the inertness of the halide.

When 2.0 g. was treated with sodium in dry ether for two days (the solvent was refluxed for five hours during this period), 1.985 g. was recovered unchanged and the aqueous solution of the residue insoluble in

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[13] Ref. 4 b, p. 146.

[14] (a) Tiffeneau, *Bull. soc. chim.*, [4] 1, 1205 (1907); (b) Stieglitz and Leech, THIS JOURNAL, 36, 272 (1914); Stieglitz and Vosburgh, *Ber.*, 46, 2151 (1913); Vosburgh, THIS JOURNAL, 38, 2081 (1916).

[15] Prepared by the method of Hell and Wiegandt, Ber., 37, 1431 (1904).

[16] These reactions are being studied further and details will be published later.

ether gave no test for halogen, proving that no reaction had occurred. A similar experiment employing boiling toluene as a solvent was continued for ten hours but precipitation of silver chloride from the aqueous extract indicated that but 1.88% of the material had reacted.

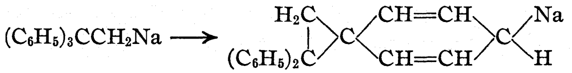
However, even these facts may have some bearing upon the mechanism of the reaction. Since there is no doubt that sodium could react readily and completely with any hydrogen chloride liberated under the conditions described, any loss of hydrogen chloride from the halide must be very slight in ether at 35° and toluene at 111°. If reaction is assumed to take place according to Mechanism II, it is also necessary to make the doubtful assumption that the cleavage of the halide, which is sufficient for complete reaction in ammonia at −33.5°, is decreased to almost nil by raising the temperature to +35° and then increased again by further raising the temperature to 111°. On the other hand, Mechanism I permits the differences in reactivity of the halide to be ascribed to variations in the influences favoring the reaction of the sodium. This is in accordance with the facts, for the conditions become progressively more favorable to reaction of the sodium in passing from ether at 35°, where the metal is solid and readily coated with insoluble crusts, to toluene at 111°, where the sodium is molten and continuously presents a fresh surface for reaction, and to ammonia at −33.5° where the metal dissolves and may be used at high concentrations.

The Action of Pyridine on β-Chloro-α,α,α-triphenylethane.—It has just been noted that the variation in reactivity of the chlorotriphenylethane toward sodium under different conditions casts doubt upon the validity of Mechanism II. Further light upon this problem might be expected from a study of the reactivity of this halide toward a reagent which would combine readily with any liberated hydrogen chloride but which had very little tendency to remove the halogen alone.

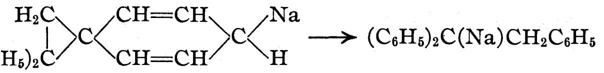
Such a reagent is pyridine and at its boiling point (115°) the conditions for cleavage of the halide would appear to be as favorable as in toluene solution. Yet when two grams of the chlorotriphenylethane was dissolved in pyridine and the solution boiled under a reflux condenser for ten hours, little evidence of reaction was obtained. A quantity of the unchanged halide was recovered and treatment of the aqueous extracts with silver nitrate produced only a barely perceptible opalescence.

It is scarcely probable that pyridine inhibits, or that toluene in any special way promotes cleavage of hydrogen chloride from the chlorotriphenylethane. Consequently, the reaction with sodium in toluene must consist of direct halogen removal and the rearrangement in liquid ammonia solution very probably proceeds according to Mechanism I.

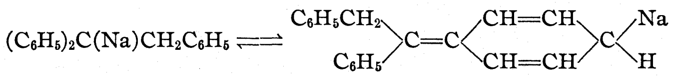
A Possible Interpretation of Mechanism I on the Basis of the Quinonoid Hypothesis.—The mechanism which has just been shown to be in best accord with the experimental evidence assumes the preliminary formation of an organo-alkali compound which then rearranges. Some reasons' for predicting such a rearrangement might be based upon the assumption that such organo-alkali compounds tend to exist in equilibrium with a tautomeric quinonoid form.[4] As pointed out in the introduction, the only type of quinonoid tautomer possible in this instance is one involving the formation of a trimethylene ring.


(12)

This structure could evidently revert to a benzenoid form in two ways, one being the reverse of Equation 12 and the other that represented below.


(13)

The stability of such organo-alkali compounds appears to be increased by the presence of phenyl groups upon the carbon atom to which the alkali metal is attached[5,6,17] and, therefore, it might be predicted that the process represented by Equation 13 would predominate over the reverse of that expressed in Equation 12. The fact that the rearranged compound could conceivably form a normal quinonoid tautomer


(14)

would perhaps also hinder the reversal of Reaction 13. Thus the sum of Reactions 12 and 13, proceeding in the direction which has just been suggested as the most probable, would constitute the rearrangement as expressed in Equation 4.

Summary

1. The action of sodium on β-chloro-$\alpha,\alpha,$a-triphenylethane in liquid ammonia leads to a molecular rearrangement.

2. Two very different mechanisms are suggested for this rearrangement and evidence is presented to discriminate between them.

3. A possible interpretation of the more probable mechanism on the basis of the quinonoid hypothesis is outlined.

CAMBRIDGE, MASSACHUSETTS

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[17] Schlenk, Appendrot, Michael and Thal, *Ber.*, **47**, 473 (1914).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

A RELATION BETWEEN THE MOLECULAR WEIGHTS AND MELTING POINTS OF ORGANIC COMPOUNDS

BY J. B. AUSTIN

RECEIVED AUGUST 23, 1929 PUBLISHED MARCH 6, 1930

The recent paper of Hildebrand and Wachter[1] focuses attention once more on the need for some expression which will aid in a critical selection of the best values for the melting points of organic compounds. Longinescu has given the following formula[2]

$$\left(\frac{T}{10\,D}\right)^2 = n \qquad (1)$$

where n is the number of atoms in the molecule, D is the density and T is the melting point on the absolute scale. This relation is only partially satisfactory, however, for it does not involve the molecular weight directly, and is not sufficiently sensitive for critical use; hence it was decided to attempt to derive an equation involving the molecular weight and melting point directly and possessing considerable sensitivity.

In considering relations with which to start, the well-known formula of Lindemann[3] for determining the characteristic vibrations of the atoms in a monatomic solid suggested itself as a plausible beginning. This equation is of the form

$$\nu = \text{const.} \sqrt{\frac{T}{MV^{2/3}}} \qquad (2)$$

where ν is the frequency of the vibration, T is the absolute melting pcint, M is the atomic weight and V is the atomic volume. In the derivation of this expression several simplifying assumptions are introduced: it is assumed that the atoms of the solid are arranged in cubes, that their vibrations are simple harmonic and that the Law of Dulong and Petit is valid. In spite of these rather limiting assumptions the result as given above is in agreement with experimental evidence as Grüneisen has shown.[4] The vibrators postulated by Lindemann are merely spherical bodies and might with equal validity be considered as polyatomic molecules. In this case ν would be the molecular vibration frequency, V the molecular volume and M the molecular weight. Solving for M we obtain

$$M = \text{const.} \frac{1}{\nu^2} \frac{T}{V^{2/3}} \qquad (3)$$

At this point we may hazard a guess that for most organic substances ν is of the same order of magnitude, while for substances of related struc-

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[1] Hildebrand and Wachter, THIS JOURNAL, 51, 2487 (1929).

[2] Longinescu, *J. chim. phys.*, *1*, 296, 391 (1903).

[3] Lindemann, *Physik. Z.*, 11, 609 (1910).

[4] Grüneisen, *Ann. Physik*, 39, 296 (1912).

ture it should be almost the same. Aside from expecting such an assumption to hold as a result of general experience in the similarity of physical properties of related organic molecules, we have an indication of its existence in the so-called "Crompton–Walden Rule" which relates the heat of fusion and the absolute melting point, as follows

$$\frac{\Delta H_F}{T_F} = \text{const.} \tag{4}$$

The heat of fusion, being roughly a measure of the work required to separate the molecules, must be, in some measure, a criterion of the magnitude of the molecular vibrations, and especially is this true near the melting point. The constancy of this ratio indicates, therefore, that in corresponding states most organic materials have nearly equal molecular vibrations. The ν in Equation 3 may, therefore, be included in the constant term. Moreover, V may be expressed in terms of M, D_m, the density at the melting point, and Avogadro's number. Making these changes in Equation 3, we obtain

$$M^5 = C' D_m^2 T^3 \tag{5}$$

or

$$\log M = C + \frac{3}{5} \log T + \frac{2}{5} \log D_m \tag{6}$$

where C is a new constant.

However, the density as usually measured is not the density at the melting point but the density at room temperature. These densities are related by the expression

$$D = D_m(1 + \alpha t) \tag{7}$$

where α is the coefficient of cubical expansion and t is the difference between the melting point and room temperature. For organic solids not many data are available but α seems to have a value of about 0.00025. Since t is usually not very large, this correction is, in general, negligible. For liquids we may take α as 0.0011 without introducing considerable error. Here again t is small, so that the correction term will be insignificant, especially as compared with errors introduced by other approximations. Thus, for the present purpose, D and D_m may be taken as equal. Hence our desired expression is

$$\log M = \text{const.} + \frac{3}{5} \log T + \frac{2}{5} \log D \tag{8}$$

We may now proceed to test our equation: first in a case where the density term is negligible and second in a case where it must be considered.

It will be observed that the constants for benzene and toluene are lower than the others; this abnormality seems to be typical of the first members of a series and has been discussed by Smyth in connection with electric moments.[5]

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[5] Smyth, THIS JOURNAL, 51, 2380 (1929).

TABLE I

AROMATIC HYDROCARBONS

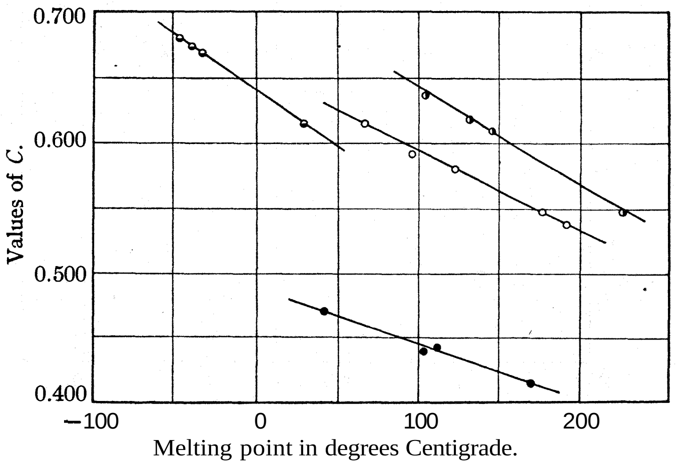
Substance	T_m	D	*M*	**Const.**
p-Xylene	286	0.861	106	0.551
Benzene	278	.878	78	.432
o-Xylene	246	.879	106	.580
m-Xylene	215	.865	106	.625
Ethylbenzene	180	.868	106	.672
Toluene	178	.866	92	.642

TABLE II

MONOSACCHAROSES

Substance	Tm	D	*M*	**Const.,** neglecting D	**Const.,** corrected **for** D
Levulose	377	1.669	180	0.705	0.637
d-Mannose	405	1.540	180	.695	.620
d-Glucose	419	1.544	180	.685	.610
Dambose	497	1.752	180	.645	.548

It will be seen at once that while the constants for each class of material are of the same order of magnitude, they vary considerably within the class. This variation, which probably arises from the assumption that v is constant, is emphasized by the logarithmic form of the function. If, however, *C* is plotted against T for each class, the points fall on a straight line as shown in Fig. 1, in which the lines shown are picked at random from a number of such lines used in testing the equation.



◑, Monosaccharoses; ○, aromatic acids; ◒, aromatic chlorides; ●, aromatic alcohols.

Pig. 1.

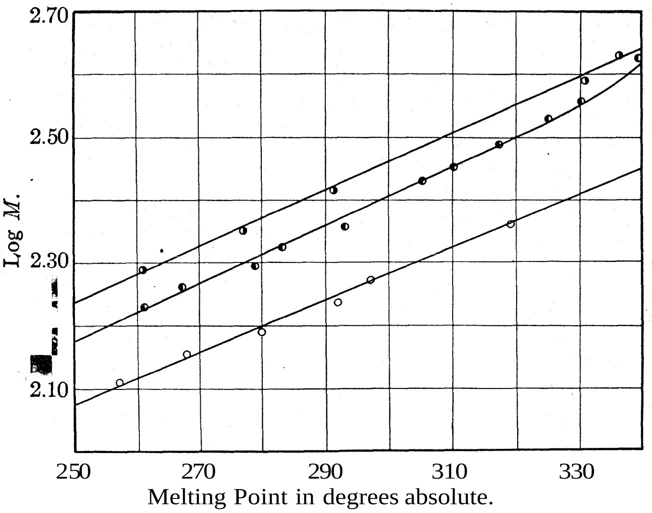
This linear variation of the "constant" with temperature means that Equation 8 should read

$$\log M = A' + BT_m + \frac{3}{5}\log T_m + \frac{2}{5}\log D \tag{9}$$

The introduction of the term in T seems to add to the complexity of the expression but by making a few approximations we may greatly simplify it. Thus D is nearly unity for a great many organic substances, hence log D approaches zero and the term involving it may be neglected. Moreover, a variation in T from 100 to 600 on the absolute scale causes the term in log T to vary from 1.2 to 1.6; since this extreme variation in T produces such a small effect we may, as a first approximation, combine the first and third terms on the left side of (9) to obtain

$$\log M = A + BT_m \tag{10}$$

This equation is found to represent the observed data with considerable accuracy, as the curves in Fig. 2 show. The line for the normal paraffins shows the greatest curvature but even this is small enough so that the linear relation may be assumed to hold over a limited range.



O, Aliphatic alcohols; ◑, olefins; O, normal paraffins.

Fig. 2.

Curves of this sort are chiefly useful in a critical examination of recorded data. For example, in the case of dicetyl, discussed by Hildebrand and Wachter, the use of the value of 75°, given as the melting point in the "International Critical Tables," throws the point for dicetyl considerably off the curve, whereas the value of 70° selected by them gives a point which falls nicely on the curve. Another application is the calculation of melting points which have not been experimentally determined. There are numerous series of homologs for which the melting points of but 3 or 4 members have been determined. These 3 or 4 points are, however, sufficient to allow the construction of a curve from which the melting point of any compound of the series may be easily read off.

From a study of a number of such curves it would appear that the lines for straight-chain paraffins and their simple derivatives, such as the alcohols, have the same, or very nearly the same slope; hence a common value of B may be given which defines a family of lines. This value of B is **0.0040** and the family of lines may be represented by the equation

$$\log M = A + 0.0040\,T \qquad (11)$$

For such a family, data for a single member of a given series will serve to determine *A* and fix the line for that series. With branched chain and cyclic compounds the slopes are in general different. In many cases the slope has a negative sign; this is true of the series given in Fig. 1, since the "constant" lines have a negative slope and the slope of Equation **10** is the same as for the "constant" lines.

It should be mentioned in conclusion that Equation **10** applies only to true homologs; a series such as the normal paraffins has one curve, the secondary paraffins another. Complete failure results if an attempt is made to include isomers of the ortho–meta–para type in one curve.

Summary

A relation between the melting points and molecular weights of organic homologs has been derived. It is particularly useful in a critical examination of melting point data.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, MCGILL UNIVERSITY]

THE ADSORPTION OF WATER BY WOOD

BY LLOYD M. PIDGEON AND O. MAASS

RECEIVED AUGUST 20, 1929 PUBLISHED MARCH 6, 1930

Variation in the amount of adsorbed water in wood has a definite effect on many of its physical properties, such as swelling, strength, etc. In spite of the practical importance of these properties few determinations have been made of the adsorption of water by wood and cellulose throughout an extended range of vapor pressure and temperature. Even fewer determinations have been conducted by methods free from inherent error.

In this paper a method is detailed whereby the adsorption of water by various samples of coniferous woods and pure cellulose has been examined throughout the complete range of vapor pressures and between the temperatures of 12 and 42°. The corresponding adsorption isothermals are of particular interest from the point of view of the modern theory of gel structure.

While a considerable number of investigations on the fiber saturation point of wood have been made, the complete adsorption has rarely been produced. Tiemann,[1] Myer and Rees,[2] Dunlap[3] and Stamm[4] have determined saturation points by various methods, the method of Stamm being capable of considerable accuracy. Extensive work on cotton cellulose is due to Urquhart and Williams,[5] who have produced complete adsorption isotherms over a large range of temperature. Several investigators have noticed a hysteresis effect between the gain and loss of water. In general it has been the practice to report the two values of adsorption for each vapor pressure, though certain investigators have assumed a mean value as the true equilibrium point.

Little of the work which has been done is entirely free from objection. In even the most careful determinations of the adsorption by cotton cellulose the amount of adsorption was measured indirectly. In the case of wood, by the use of large samples the rate of establishment of equilibrium was often confused with the rate of diffusion into the interior of the block; also, the presence of air with a partial vapor pressure of water greatly inhibited the adsorption. A second objection was the possibility of liquid condensation on the sample at pressures near the saturation point. Thus by a combination of these factors McKenzie[6] was able to report a saturation value of 43.2% after seventy-nine days with "adsorption" still slowly taking place.

As will be seen in the following, the time to equilibrium has been reduced to a reasonable duration by removing all gases other than water vapor from the apparatus, and by the use of small samples weighing no more than 0.15 *g*. Also it has been possible to obtain a direct measurement of the amount of adsorption free from error due to liquid condensation.

Experimental

In principle the apparatus employed was simply a spring balance suspended in an evacuated chamber. The required vapor pressure of water was obtained either by maintaining a known temperature in a body of water in communication with the apparatus or by direct measurement with a manometer. The amount of adsorption at any vapor pressure was obtained directly from the weight of the sample.

The apparatus is shown in Fig. **1**. The spirals were mounted in triplicate in special chambers (C, D, E) furnished with ground-glass joints. The spirals were suspended from glass hooks sealed just above the ground joint. Connecting these tubes to the

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[1] Tiemann, U. S. Dept. Agr. Forest Service Bull., 70, **82 (1906);** Forest Service Circ. **108 (1907).**

[2] Myer and Rees, New York State College of Forestry, Tech. Bull. **26,** No. 19 **(1926).**

[3] Hawley and Wise, "The Chemistry of Wood," p. **286,** data of **M. E. Dunlap,** U. S. Forest Products Laboratory **(1929).**

[4] Stamm, *Ind. Eng. Chem. Anal. Ed.,* **1,** 94 **(1929).**

[5] Urquhart and Williams, *Shirley Inst. Mem., 49,* **197, 307 (1924).**

[6] Hawley and Wise, "The Chemistry of Wood," McKenzie, unpublished report U. S. Forest Products Lab.

pumping system was a phosphorus pentoxide tube (G). To supply water vapor to the apparatus a tube was placed at (B) filled with water which had been carefully freed from all dissolved gases by freezing and evacuating several times. The stopcocks connecting these parts of the apparatus were of large bore to reduce to a minimum the time required to establish a constant vapor pressure throughout the apparatus. The tubes containing the spirals were immersed in a glass-sided thermostat fitted with a thermoregulator giving temperature control to ±0.01°. By means of a cooling coil a temperature range of from 10 to 42° was obtainable.

Deflections of the spiral were measured by means of a cathetometer accurate to 0.05 mm. Before each reading of the deflected end of the spiral the position of the fixed end was taken as a reference point. In this way it was possible to obviate any error due to displacement of cathetometer or apparatus between readings.

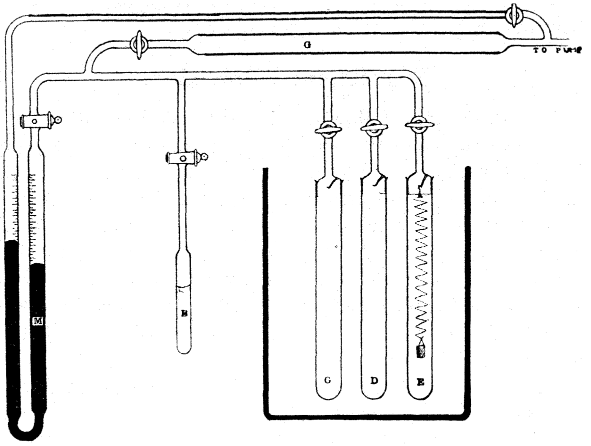

Fig. 1.—Adsorption apparatus

Spirals were constructed of quartz after the manner of McBain and Bakr[7] by drawing fibers from a rod of silica and winding them on a carbon rod by softening the appropriate point with a small flame. The spirals employed in this investigation were considerably finer than those previously described and the most convenient flame for bending them proved to be a small gas jet without internal air supply. This flame is sufficiently hot to soften the fiber without danger of fusing it off, a frequent eventuality if any type of blast is employed.

The balance was calibrated throughout the working range by noting the deflections caused by known weights. The curve obtained by plotting deflection against corresponding weight was in all cases a straight line generally passing through the origin. The three spirals which were employed indicated a deflection of 1 mm. when supporting weights of 0.0023, 0.0022 and 0.0033 g., respectively. Thus, with the cathetometer employed, a weight of 0.0001 g. could be detected, and the total weight of a sample weighing 0.1 g. could be determined accurately to 0.1%. Since the maximum differences noted in this investigation were from 20 to 30% of the total weight, the theoretical accuracy was within 0.5% of the differences noted.

The pumping system consisted of a mercury vapor condensation pump backed by a Töpler pump. A McLeod gage was used to indicate the pressure.

To measure the aqueous vapor pressure a manometer was employed filled with

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[7] McBain and Bakr, THIS JOURNAL, 48,694 (1926).

"Cenco" pump oil. This oil has a negligible vapor pressure and gives a deflection some fourteen times that of mercury. In a later form of the apparatus the manometer was immersed in the thermostat so that all the connecting tubing was maintained at a constant temperature. In this apparatus the oil manometer was replaced by a short mercury manometer, the loss in sensitivity being compensated for by reading the levels with the cathetometer.

SAMPLES.—Only coniferous woods have been examined, and in particular: spruce (Picea canadensis), both green wood and dry wood; pine (*Pinus* banxiana), green wood; purified cotton cellulose. In the case of the wood samples a standard thickness was chosen of 1.5 mm. in the longitudinal direction. In such a sample every fiber is cut through at least once, so that all of the fiber cavities are exposed and the rate of adsorption will be unaffected by the rate of diffusion through the wood structure. Finely ground wood meal has been examined and found to give exactly the same rate and final value, giving experimental confirmation to this idea.

Experimental Procedure

Two general methods were followed. **1.** Indirect Measurement of Vapor Pressure.—To perform an experiment the samples were suspended from the spirals and the ground joints lubricated and set in place. The pumping system was then actuated for twelve hours, at the end of which time the pressure had fallen to 0.0003 mm. of mercury and the sample had reached a constant dry weight (see later). The deflection of the spirals was then noted and the weight of the sample calculated. The tube (B) was then immersed in a flask maintained at any desired temperature, the corresponding vapor pressure of which was obtained from tables. Readings of deflection were taken until the sample had reached a constant weight. At pressures considerably below the saturation pressure this constant weight is attained in less than half an hour (see Fig. 3), though two hours was allowed to elapse to ensure complete establishment of equilibrium. The final deflection of the sample gave its weight, from which the amount of adsorption could be calculated knowing the dry weight. The temperature of tube (B) was then raised and the adsorption measured at the correspondingly higher vapor pressure. In this way the range of vapor pressures from zero to the saturation value may be investigated. This method is particularly applicable to the measurement of rates of adsorption, as several samples may be examined concurrently under identical conditions of pressure and temperature.

2. Direct Measurement of Vapor Pressure.—The sample is dried as in Method 1, after which a small amount of water vapor is added by momentarily opening the tap to tube (B). The pressure will be indicated on the oil manometer, which will fall from its initial value as water is adsorbed by the wood. The attainment of equilibrium is indicated by a constant pressure on the manometer. At this point the weight of the sample is found as before and the corresponding vapor pressure read directly on the manometer. A much longer time is required by this method as the pressure falls off as adsorption increases, while in the first method the pressure is maintained by the water tube, which acts as an inexhaustible reservoir. While theoretically there is no reason why several samples should not be in communication with the same manometer, it has been found practically that if more than one sample is examined at once, great time is required for the re-adjustment of equilibrium between the samples. This method is convenient in that it requires little personal attention.

By either of the methods outlined above it is possible to obtain desorption values, that is, values obtained by the loss of water from a more saturated condition. Also, by placing a little free water in the tubes with the samples, it is possible to remove the air by pumping without completely drying the samples. For vapor pressures near the saturation point Method 1 is particularly valuable, as it will be seen that as long as the temperature of tube (B) is slightly below that of the thermostat, liquid condensation cannot take place on the sample. In this way it is possible to approach closely the saturation point.

Dry **Weight of** Samples.—Throughout this investigation the dry weight of wood has been taken as the weight of a sample when highly evacuated in presence of phosphorus pentoxide at ordinary temperature. It has been found that under such conditions the point of equilibrium is reached in at least twelve hours. This point is completely reproducible and may be checked several times even after the adsorption of water. Any further moisture which might be driven off by heating may be considered as chemically combined, as it is held at zero vapor pressure under the conditions of the experiment and would not appear on the isothermals.

Experimental Results

In recording the experimental results only those which are essential to illustrate the order of accuracy will be given. A large number of observations have been made but where these are identical they have been omitted.

Adsorption by Spruce Wood.—In the following table are shown the adsorption values at 23° corresponding to various vapor pressures. Each of these values was obtained by loss of water from a drier state (see later, "Hysteresis").

TABLE I

EQUILIBRIUM ADSORPTION VALUES FOR SPRUCE SAPWOOD AT 23°

V. p., mm. of mercury	1.95	4.58	9.21	10.51	12.78	15.51	17.45	20.40
Relative humidity, %	9.26	21.72	43.75	50.31	60.68	73.82	83.22	97.13
Adsorption, %	2.7	5.1	9.5	10.1	12.3	13.8	14.1	20.0

A similar set of values for both spruce heartwood and sapwood was obtained at temperatures between 12 and 42°. In order to conserve space these values are not tabulated but the results for sapwood are plotted in Fig. 2. It has been found that the final values attained by heartwood and sapwood at any given vapor pressure are approximately the same. The following typical set of values at 29° will illustrate this fact.

Heartwood	0.7	1.2	2.2	2.8	3.9	7.5	8.9
Sapwood	0.8	1.3	2.3	2.8	3.8	7.5	8.7

When plotted, these values lie on the same curve, so from the point of view of final equilibrium value the distinction between heartwood and sapwood drops out. This has been found to be the case in all of the woods examined in this investigation.

The final equilibrium is generally reached from the dry state in under half an hour in the case of moderate vapor pressures. No further change is noted from this value after the lapse of twenty-four hours. The attainment of equilibrium by desorption, or loss of water from a more saturated condition, is a more lengthy process, several hours being necessary for complete equilibrium. This is illustrated in Fig. 3, where the adsorption is plotted against time. At vapor pressures near the saturation point the time required for equilibrium in either direction is considerably greater than the values mentioned.

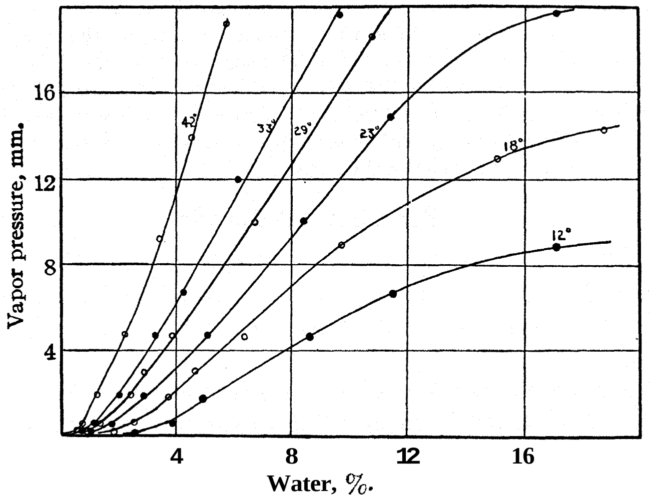

Fig. 2.—Adsorption isothermals of spruce wood.

In practically all cases a definite hysteresis effect was found. A large number of experiments have established this as a permanent effect and not simply due to incomplete equilibrium (see Fig. 3). In Fig. 4 the adsorption and desorption curves are indicated for spruce (S) and cotton cellulose (C). The hysteresis effect disappears before the origin is reached, as shown in the same figure (B), where the lower part of the curve for spruce has been plotted on a larger scale. Based on theoretical considera-

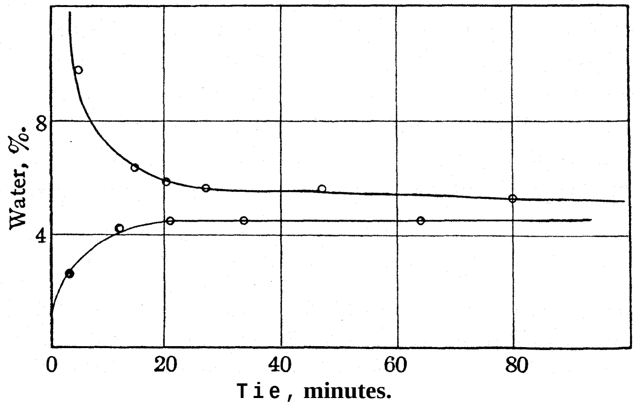

Fig. 3.—Adsorption–time curves.

tions to follow, the lower, or desorption, curve is considered to represent the true equilibrium value at any stated pressure; hence in all cases where it is not specifically stated otherwise the equilibrium adsorption value refers to the desorption value. As this desorption process is inconveniently long, a method has been developed of reaching the true value by adsorption. In a typical case, that of spruce wood at 23° and a vapor pressure of 4.58 mm. of mercury, the value reached by adsorption is 5.5%. Under the same conditions of temperature and pressure the desorption value is 6.0%, indicating the well-marked hysteresis. If, however, from a more saturated condition (*i. e.*, more than 6%) the sample is rapidly dried below the final value (to about 3%) and again exposed to a vapor pressure of 4.58 mm., the higher value of 6.0% will be rapidly reached by ***adsorption.*** This procedure is easily carried out in the apparatus by alternately opening the taps to the drying tube and the water tube, the latter being maintained at the required temperature. This procedure has an important bearing on the theoretical discussion to be set forth in a later section.

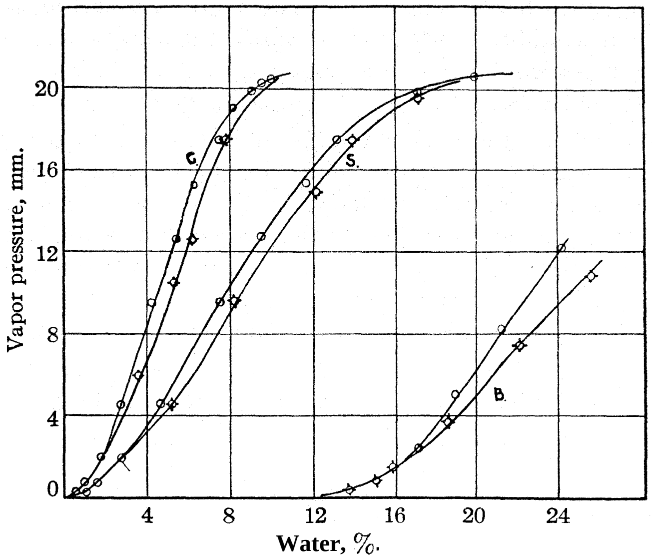

Fig. 4.—Adsorption isothermal at 23°. *C*, Cotton cellulose; S, spruce wood; B, S enlarged.

Effect of Drying.—While the above results were obtained with green wood, a number of measurements have been carried out on wood which has been dried in the open for some time (at least one year). A few of the results obtained are reproduced below together with comparative results for green wood.

At lower vapor pressures there is apparently no difference between the two woods, while at higher pressures the air-dried sample shows much

TABLE II

ADSORPTION VALUES FOR GREEN AND DRIED SPRUCE WOOD

Vapor pressure, mm.	4.58	9.21	12.78
Adsorption, green	5.0	9.7	11.8
Adsorption, dried	5.0	6.9	9.3

lower adsorption. This behavior may be regarded as typical in that if differences are noted they will be greatest in the region of the saturation point.

The effect of long-continued drying is to lower the value reached by adsorption. Thus in the following case of pine wood the sample was first dried, after which it was exposed to a vapor pressure of 4.58 mm. of mercury. When equilibrium had been attained, the sample was re-dried and the process repeated. The results obtained were as follows

1st adsorption, 5.2%	2nd, 5.1%	3rd, 4.8%

If, however, at any time the sample is subjected to a higher vapor pressure such as near the saturation point, the wood seems to be restored to its original adsorptive power. Thus in the following case the sample was dried and exposed to various higher pressures of water, and it is evident that the value at 4.58 mm. (33°, spruce wood) obtained between these steps shows no decrease in magnitude.

(1) 3.4%	(2) 3.4%	(3) 3.6%	(4) 3.5%

Adsorption by Pine Wood.—In Fig. 5 the adsorption curve at 23° for pine is shown together with that of spruce. As in the case of the spruce, a definite hysteresis was noticed, and as in the previous case, the lower value is reported. Heartwood and sapwood also show little difference in adsorptive power. The fiber saturation point obtained by extrapolation of the isothermal at 23° is 31%, which may be compared with a value of 24% for spruce.

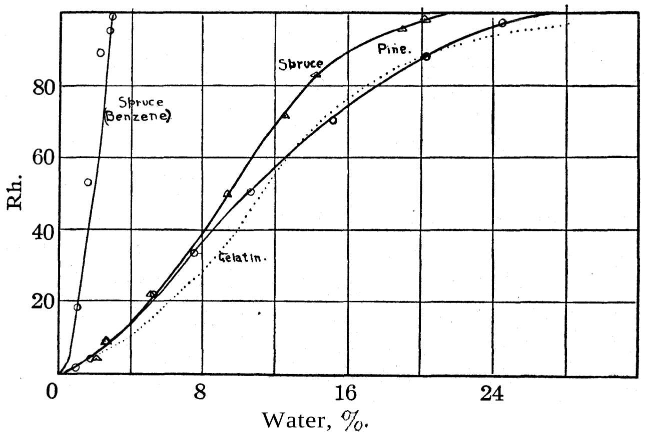

Fig. 5.—Adsorption isothermal, at 23°.

Adsorption **by** Cellulose.—In all cases a sample of purified cotton cellulose was examined concurrently with the wood. The values obtained are considerably lower than for wood, the saturation point obtained by extrapolation being 11%. Extracted wood cellulose, prepared by laboratory methods such as that in the analytical determination, yielded much higher values than wood, as will be seen in Table III, in which are recorded results obtained by the adsorption of water from the dry state.

TABLE III

ADSORPTION VALUES AT 23° OF SPRUCE WOOD, EXTRACTED CELLULOSE AND COTTON CELLULOSE

V. p.	Spruce	Extr. cellulose	Cotton cellulose
0.22	0.9	1.5	0.5
0.77	1.6	[1.9	1.0
1.95	2.7	3.5	1.8
4.58	4.7	(5.4	2.7
9.21	7.3	8.1	3.6
12.78	9.5	11.1	5.5
15.78	11.7	13.1	6.7
17.45	13.2	14.5	7.5
19.20	15.3	18.0	8.2
19.80	17.1	18.9	9.0
20.65	20.2	23.0	9.9

Rate of Adsorption.—It has been found that the time required to establish equilibrium increases with the vapor pressure, as indicated in the following table.

TABLE IV

RATE OF ADSORPTION

Temp., 33° V. p., 0.1 mm.		Temp., 33° V. p., 4.58 mm.		Temp., 23° V. p., 18.11 mm.	
Time, min.	Adsorption, %	Time, min.	Adsorption, %	Time, min.	Adsorption, %
1.0	0.1	1.5	1.25	2.0	3.7
3.5	.2	4.5	1.4	7.0	6.3
9.0	.3	8.5	2.3	15.0	8.4
Final	.3	14.5	3.0	32.0	11.1
		21.5	3.2	67.0	13.5
		Final	3.2	195.0	15.8
				300.0	16.3
				Final	16.42

Nature of Vapors.—While in the majority of cases the adsorbate has been water vapor, one experiment has been performed using benzene. The results are plotted in Fig. 5 and will be discussed subsequently.

An experiment was performed on a sample of lignin supplied by the Department of Cellulose Chemistry of this University. At 23° and a vapor pressure of 4.58 mm. of mercury, the value obtained was 2.1%, which may be compared with 4.7% for spruce wood under the same conditions.

Discussion of Results

Variation of Adsorption with Vapor Pressure.—Figure 4 (S) representing the adsorption isothermal of spruce wood at 23° may be taken as the typical curve relating adsorption to corresponding vapor pressure. This smooth s-shaped curve is at once recognizable as typical of the adsorption of a vapor which is condensable to a liquid which wets the adsorbent. Three general divisions of the curve may be indicated, The first 1–2% of water is apparently highly adsorbed, causing a lowering of vapor pressure which brings about a flattening of the curve near the origin. From an adsorption of 2 to 10% the curve follows what is practically a straight line, indicating that in this portion adsorption is proportional to pressure. As the saturation pressure is approached, the curve again flattens out, becoming asymptotic to the axis of adsorption, so that in this region a small increase in vapor pressure will cause a great increase in adsorption. The shape of the curve near saturation demonstrates the difficulty of obtaining an accurate value for the fiber saturation point by direct measurement of water content; in fact, from this standpoint, no such sharply defined point exists. These different parts of the curve have a theoretical significance which will be brought forward later.

Variation of Adsorption with Temperature.—The effect of variation in temperature on adsorption is indicated in Fig. 2. In common, with the general case, adsorption decreases with rise in temperature. On the other hand, at more elevated temperatures the vapor pressure required to produce the same relative humidity will be greater. In fact, the increase occurs in the same ratio that adsorption falls off. This may readily be seen in a qualitative way: the adsorbed water exhibits a vapor pressure which is a constant fraction of that of pure water, so that as temperature increases the vapor pressure of the adsorbed water will be proportionately the same as that of a plane water surface at the same temperature. Since the vapor pressure of adsorbed water and the amount of adsorption are in a sense inversely proportional, the amount of adsorption will decrease with rise in temperature in the same ratio as the vapor pressure of water increases. Hence it follows that if the relative humidity be kept constant, adsorption will be independent of temperature.

Practically it is found that this is not entirely the case. In Fig. 6 the isotherms of Fig. 2 have been plotted on the basis of relative humidities in place of absolute vapor pressures. It will be seen that the lower temperatures show higher adsorption.

Adsorption **Isosteres.**—If the vapor pressures corresponding to a given amount of adsorption are plotted against temperature, an adsorption isostere is produced. Such a curve represents the variation of vapor pressure with temperature for a given amount of adsorbed water. From what has been said above it is evident that the isostere will be an exponential curve similar to the typical vapor pressure curve. Thus if log p is plotted in place of pressure the resulting graph should be a straight line. This procedure has been followed in Fig. 7, and it is apparent that such a line is produced for isosteres representing an adsorption value above 2%. Below this value the lines become convex to the pressure axis. These curved isosteres fall in the region where, as mentioned previously, the adsorption isotherm shows a discontinuity which is probably caused by the introduction at this point of some new factor in the mechanism of adsorption. It would be expected that isosteres near the saturation point would also exhibit anomalous behavior, but a sufficient number of experimental values in this region are not available.

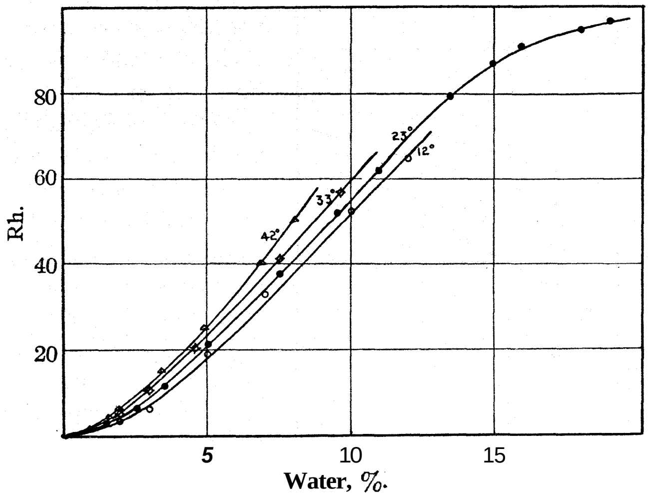

Fig. 6.—Variation of adsorption with temperature.

From purely theoretical reasoning Williams[8] has developed an isosteric equation of the form

$$\log a/c = B + AT$$

where c is the equilibrium concentration outside the adsorbent, a the amount of adsorption, T the absolute temperature, and A and B are functions of a but not of T. This equation has been shown to be applicable to the isostere of cotton cellulose by Urquhart and Williams (*ibid.* p. 1). The concentration, c, is replaced by pressure and the equation becomes

$$\log a/c = B' + AT$$

Since a is constant for any isostere, B' and A are also constant, so that if log p is plotted against $1/T$ the resulting graph should be a straight line. The results for spruce wood when submitted to this procedure

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[8] **Williams,** ***Proc.*** **Roy.** *Soc.* London, **96A,** 297 (1920).

give curves similar to Pig. 7, that is, a discontinuity is noticed for isosteres representing adsorptions less than 2%, while for a large part of the isotherm the results may be represented by a general equation.

Moisture Equilibria of Pine (*Pinus banxiana*).—In Fig. 5 the comparison between spruce and pine brings out the fact that while the two woods differ widely near the saturation point for a considerable distance above the origin, the two curves are identical. This is probably the typical behavior with many woods, as the lower part of the curve deals largely with true adsorption on the fundamental wood substance, which is probably similar in all species. The variation near the saturation point is probably due to differences in the larger structure of the wood, such as would exist between the different species.

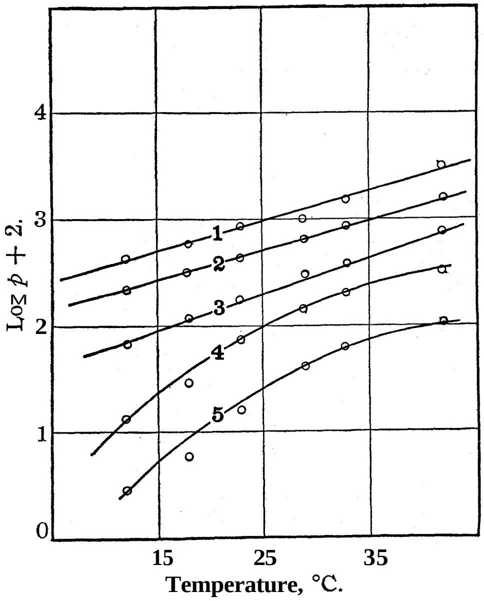

Fig. 7.—Adsorption isosteres: 1, 8%; 2, 5%; 3, 3%; 4, 2%; 5, 1%.

Moisture Equilibria of Cotton Cellulose.—The adsorption values for pure cotton cellulose are considerably lower than for wood (see Fig. 4C.). This difference is more definite than any that has been noticed between different species of wood, as the adsorption curves do not coincide over any portion of their length. Since the non-cellulose parts of wood do not show high adsorption (see lignin), this difference in adsorption is probably due to a difference in character between the cotton cellulose and the wood cellulose. Several explanations of this difference are possible. Cotton cellulose is considered to be similar to the a-cellulose of wood, *i. e.*, it is insoluble in 17.5% caustic. Hence the presence of the additional β- and y-celluloses, which are soluble in alkali of the above concentration, may account for the higher adsorption of wood cellulose. The solubility of β- and y-cellulose in alkali is evidence in favor of an increased affinity for water.

The difference in character between cotton cellulose and wood cellulose may be characterized by a coarser gel structure which brings about a lower adsorption. Again, it is possible that the presence of waxes in cotton may be the cause of an altered surface which has an effect on adsorption. The fact that the adsorption curves do not coincide in any part would indicate a difference in chemical attraction rather than a physical difference in structure.

General Discussion

In general a condensable vapor may be taken up by a solid by adsorption, by liquid condensation and by absorption or solution. While it is possible that all these mechanisms play a part in the adsorption of water by wood, the results of this research may be well explained by assuming a combination of adsorption and condensation based on the prevalent ideas of adsorption by gels. In Fig. 5 a comparison has been made between the adsorption isothermal of gelatin and that of wood. The similarity is at once apparent, so that with some justification cellulose may be classed with gelatin as a swelling gel.

It is generally assumed that gels possess a heterogeneous structure in which the actual particles of the gel are separated by small ultra-microscopic spaces or capillaries. No assumptions are necessary as to the shape of the particles or micelles (such as fibrillar or granular). When the dried gel is brought in contact with a condensable vapor, the great surface which is presented by its internal structure is saturated by adsorption of the vapor. As the external vapor pressure is increased, a point is reached at which liquid appears in the small capillaries, held at reduced vapor pressure by the great curvature of surface. Further adsorption of water takes place by the filling of these capillary spaces. In the case of non-swelling gels the micelles become rigid on desiccation; hence, when again brought into contact with water, they take it up only in so far as they fill the capillary spaces which remain a constant size. Thus in the case of non-swelling gels liquid is taken up at a constant vapor pressure until saturation is reached. In the case of swelling gels, on the other hand, the micelles do not lose their power of taking up liquid reversibly. That is, when liquid is again added, the micelles move apart from the packed condition which was assumed on drying and the whole gel swells. This process is characterized by an increase in the size of the intermicellular spaces which, in turn, causes an increase of vapor pressure. Thus a swelling gel takes up water with increase of vapor pressure until saturation is reached, at which point the vapor pressure will be the same as that of a plane water surface.

This picture may be applied to the present case to give a theoretical explanation of the adsorption isothermal. Dry cellulose may be considered as a desiccated colloidal gel consisting of a great number of particles. These particles may be the cellulose molecules themselves or aggregates of molecules. (Herzog, by x-ray measurements, has calculated the volume of the cellulose molecule as $0.68\mu^3$. Micellular particles are generally larger than this.) The micelles are probably orientated in the cellulose fiber, as swelling is not uniform in all directions. Owing to the fineness of the particles the surface presented will be enormous. Stamm has calculated the surface per gram of wood to be 310,000 sq. cm. On this surface the vapor is first adsorbed, the pressure exerted by the water molecules being less then the saturation value by virtue of the attraction between water molecule and cellulose micelle. The amount of water required to saturate this surface will be taken up rapidly by the process of true adsorption of a gas on a solid, and for any given vapor pressure the equilibrium adsorption value may be attained in either direction, that is, there is no hysteresis effect. This is well shown, in the case of wood, by the shape of the adsorption isothermal near the origin. The first 1 to 2% of water is taken up reversibly and at a reduced vapor pressure, causing a flattening of the curve in this region.

As more water is added, eventually the opposing surfaces will unite to form a column of water in a capillary. The pressure at which this takes place will depend on the diameter, the largest capillaries being the last to fill. When this takes place, there is practically a free water surface in the gel, the vapor pressure of which is governed by the radius of curvature of the capillaries. As more water is added the capillaries fill and, as cellulose is a swelling gel, the micelles move apart, causing an increase in the radius of curvature of the water surfaces. Hence vapor pressure increases with adsorption and from the curves it will be seen that this takes place in a linear fashion.

As the vapor pressure approaches the saturation point, a very small lowering will be sufficient to cause liquid condensation. Hence it is conceivable that larger pores in the wood are becoming filled with liquid. Due to the large size of these pores a small change in vapor pressure will entail a great difference in the amount of adsorption, and the curve which expresses this will flatten out.

Further evidence in favor of this view is adduced from a consideration of the rates of adsorption at different vapor pressures (see Table IV). If dry wood adsorbs water vapor at a pressure of 0.1 mm. of mercury, the time required for the establishment of equilibrium is approximately nine minutes. This value is of an order of magnitude comparable with the usual rates of adsorption, which seldom exceed several minutes. Along the straight portion of the curve the time required to establish equilibrium is approximately twenty minutes, a value which increases at higher pressures. According to the idea submitted above, the increase in time over the case for pure adsorption will be due to the time required to fill the capillary spaces between the micelles of the wood. This time will depend on the rate of condensation and the rate at which the vapor diffuses to the condensing surface. For the upper part of the curve near the saturation point the time required is very great, the establishment of equilibrium being incomplete even after the lapse of several hours. This is again due to the time required to fill the large capillaries and the time required for gaseous diffusion. This latter factor is probably a very considerable one in this region as approximately 20 liters of vapor at the temperature and pressure of the experiment are required to saturate one gram of wood (500 volumes at N. T. P.).

Thus it will be seen that this picture of the colloidal nature of cellulose affords a plausible explanation of the observed facts. The reason why the adsorption isothermals of different woods often coincide in the lower parts of the curve is apparent. The taking up of water in this region depends on the finest part of the invisible structure of the cellulose, which is probably fundamentally the same in all species of woods. Condensation near the saturation point depends on the filling of the coarser, but still amicronic structure of the wood, which would be expected to vary widely between the different species. Hence differences in adsorptive power will be greatest in the vicinity of the saturation point.

Hysteresis.—A mechanism which offers an explanation of this phenomenon has been suggested by Zsigmondy[9] and was first applied to silicic acid gels. It is assumed that when the walls of the micelles have become thoroughly dried they are less easily wetted by the liquid. Thus, as water is again taken up, the radius of curvature of the surface is less than when water was lost, in which case the walls were already wetted by the liquid. Thus it follows that for the same content of water the radius of curvature is greater when water is lost, that is, the vapor pressure is lower. Hence wherever the adsorption or desorption of water takes place by the filling or emptying of small capillaries, a hysteresis effect will be noticed. In the present case it has been pointed out that the first water is taken up by true adsorption; hence in this region no hysteresis will exist, a fact which has been experimentally verified. For the remaining part of the curve a pronounced hysteresis exists until the saturation point is reached, at which point hysteresis presumably disappears as the radius of curvature becomes so great as to be little different from that of a plane water surface.

The natural conclusion of the above is that the true adsorption value for any given vapor pressure will be attained by loss of water since by this process the liquid makes its true angle of contact with the walls of the micelles unaffected by effects of drying.

A rather convincing piece of evidence in favor of this view point is afforded by the method which is mentioned above whereby it is possible to reach the desorption value by adsorption. If the sample is saturated at a vapor pressure which is higher than that under discussion, and then rapidly dried below this desired value, when it is again subjected to the required

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[9] Zsigmondy, *Z. anorg. Chem.*, 20, 157 (1909)

vapor pressure the desorption value will be reached by gain of water. That is, if the walls of the micelles are already wetted, no hysteresis will exist but the same value will be reached by adsorption or desorption.

Size of Intermicellular Capillaries.—If it is assumed that the pressure of the system is controlled by the curvature of water surfaces in capillaries, the pressure at any adsorption depends on the average diameter of the capillaries which are filled. Thus by the use of the formula connecting lowering of vapor pressure with curvature of surface, it should be possible to calculate the size of the capillaries. The point at which hysteresis disappears may be taken as the vapor pressure corresponding to the smallest capillary. The value for r in this region is 4.5×10^{-8} cm. Near the saturation point a value of 3.8×10^{-6} is obtained. These values are for spruce wood at 23°.

Nature of Vapor.—In the case of the adsorption of a condensable vapor the liquid of which does not wet the adsorbent, the vapor acts like a gas above its critical point, that is, no liquid condensation can take place on the adsorbent. In this case the adsorption values will be much lower and in the vicinity of the saturation point there will be no increase in adsorption. An experiment was performed using benzene vapor and wood which apparently confirms this behavior. The results are plotted in Fig. 5 and it will be seen that the curve is of a completely different form, the greatest change being in the region of the saturation point. This case is interesting as there have been few cases of adsorption of condensable non-wetting liquids.

Summary

The adsorption of water by certain coniferous woods and by cotton cellulose has been measured by a new method. The complete range of vapor pressures has been covered and adsorption isothermals produced for temperatures between 12 and 42°.

The effect of various natural factors on adsorption has been examined. Heartwood and sapwood appear to give identical values. In wood which has been dried for a long period of time the adsorption isothermals are the same at low vapor pressures but differ at the higher vapor pressures. This also applies to different species of wood.

Adsorption isosteres were shown to be represented by $\log a/c = B + AT$ for adsorptions representing more than 2%.

The form of the adsorption curve shows that wood may be classed as a swelling gel. The first part of the adsorption curve is due to surface adsorption, the rest to the filling up of the submicroscopic spaces.

The similarity in the adsorption isothermals of different species of wood in the lower parts of the curve shows that the nature and the finest part of the amicronic structure of the cellulose are fundamentally the same.

Cotton cellulose is fundamentally different from the cellulose in wood; this is brought out by the adsorption curves not coinciding over any portion of their length.

A hysteresis effect between gain and loss of water has been found, except at low vapor pressures, but the higher value attained by the loss of water is considered to represent the true equilibrium value at any vapor pressure.

By an application of modern gel theory a theoretical explanation of the observed facts is offered.

MONTREAL, CANADA

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

SALTS OF NITRILES. III. SODIUM PHENYLACETONITRILE[1]

BY MARY M. RISING AND GÉZA BRAUN

RECEIVED AUGUST 31, 1929 PUBLISHED MARCH 6, 1930

In 1927 and 1928 Rising and Zee reported the preparation, isolation and properties of the sodium salt of phenylacetonitrile, $[C_6H_5CHCN]Na$, and of α-phenylbutyronitrile,[2] $[C_6H_5C(C_2H_5)CN]Na$. Early in 1929 a further paper was published by Rising, Muskat and Lowe on the potassium salt of phenylacetonitrile.[3] In these papers certain conclusions are stated, based upon the behavior of the salts. (1) The salts exhibit tautomerism of the carbide–nitride type, analogous to the well-known tautomerism of the salts of acetoacetic ester

$$[C_6H_5CH{=}C{=}N^-]Na^+ \rightleftharpoons [C_6H_5C^-HCN]Na^+ \qquad (1)$$

$$[C_6H_5C(C_2H_5){=}C{=}N^-]Na^+ \rightleftharpoons [C_6H_5C^-(C_2H_5)CN]Na^+ \qquad (2)$$

(2) Each salt reacts in a nitride form. The evidence for this conclusion is presented in the papers named. **(3)** Each salt reacts also in a carbide form. The evidence for this conclusion is presented in the papers mentioned.

Because of the difficulties met by a number of workers who have tried to repeat Zee's work,[4] a thorough reinvestigation of the problem was undertaken by the present authors.[5] Sodium phenylacetonitrile was

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[1] The work here reported was completed by April 15, 1929, but publication was postponed out of courtesy to Professor F. W. Upson and his collaborators until they should have reported upon their recently resumed work on the same problem, upon which they have published nothing since 1922 [Upson and Thompson, THIS JOURNAL, 44, 181 (1922)]. See also THIS JOURNAL, 51, 263 (1929). These authors have just announced by an abstract a paper on the subject to be presented at the Minneapolis meeting of the Society and we feel free, therefore, to report our findings.

[2] Rising and Zee, (a) *ibid.*, 49, 541 (1927); (b) 50, 1699 (1928).

[3] Rising, Muskat and Eowe, *ibid.*, 51,262 (1929).

[4] See footnote, Ref. 2 b, p. 1699.

[5] I wish to express here my sincere appreciation of the fine technique of my collaborator, Dr. Géza Braun, International Research Fellow of Budapest, at the University of Chicago, 1926–1928. M. M. **RISING.**

first studied, as pure phenylacetonitrile is readily obtained. A summary of the work of the present authors is as follows.

(1) Phenylacetonitrile of freezing point −24° was used, its purity being further checked by its refractive index.

(2) An apparatus (diagram) was devised for the preparation of sodium phenylacetonitrile in an atmosphere of nitrogen. It is extremely important to protect the salt from air and moisture, since it is quickly decomposed by exposure to either. When brought into contact with air the salt smokes, glows and turns to a tar which slowly hardens.

(3) Sodium phenylacetonitrile was prepared by treatment of phenylacetonitrile with powdered sodium in dry ether, the reaction being carried out in an atmosphere of nitrogen. The salt was precipitated from its ethereal solution by means of ligroin, the operation being performed with complete exclusion of air. Analysis of the salt (which was always handled under ligroin or in an atmosphere of nitrogen) showed it to contain 15.79 and 15.76% of sodium (calcd., 16.53).

(4) Sodium phenylacetonitrile was found to be very soluble in ether. When prepared as just described it remains in solution in the reaction mixture, whereas the sodium cyanide formed as a by-product of the reaction (Equation 5) is precipitated and can be removed by filtration. The behavior of the salt was studied in ether solution and a number of observations were made.

(a) Cooling of the ether solution of the salt to −80° causes the salt to separate in fine large crystals. When the ethereal solution is stirred vigorously at −80°, a mass of finer crystals separates. The solid salt was not isolated under these conditions since it redissolves readily in the ether as the mixture warms up.

(b) Acidification of an ether (or aqueous) solution of the salt yielded pure phenylacetonitrile in nearly quantitative amount. No hydrocyanic acid was liberated in the treatment with acid.

$$2[C_6H_5CHCN]Na + H_2SO_4 \longrightarrow Na_2SO_4 + 2C_6H_5CH_2CN \qquad (3)$$

(c) Treatment of the ethereal solution of the salt with ethyl iodide produced a-phenylbutyronitrile in excellent yield.

$$[C_6H_5CHCN]Na + C_2H_5I \longrightarrow C_6H_5C(C_2H_5)HCN + NaI \qquad (4)$$

(5) Sodium phenylacetonitrile is fairly stable in ether solution but it undergoes a change during and following its precipitation by ligroin. The ethereal solution does not contain even a trace of sodium cyanide, but after the salt is precipitated with ligroin it gives a test for cyanide and cannot be redissolved completely in ether; nor could perfectly pure phenylacetonitrile be recovered from the precipitated salt by treatment with acid, and a low yield was obtained from it by ethylation, all in marked contrast to the behavior of the salt in ethereal solution before precipita-

tion, which has just been described. Evidently the salt is far less stable in its solid form than in solution.

(6) The reaction of phenylacetonitrile with sodium was studied quantitatively to determine the exact course of the reaction and the amount of each product formed. The details and results of this study are to be found in the Experimental Part of this paper. It is there shown that the course of the reaction of phenylacetonitrile with sodium may be summarized in the equation

$$2C_6H_5CH_2CN + 2Na \longrightarrow [C_6H_5CHCN]Na + NaCN + C_6H_5CH_3 \qquad (5)$$

It has been proved by us further that the formation of sodium cyanide and toluene results from the reduction of part (about one-half) of the sodium phenylacetonitrile by the hydrogen liberated in the action of sodium on phenylacetonitrile according to the equations

$$2C_6H_5CH_2CN + 2Na \longrightarrow 2[C_6H_5CHCN]Na + 2H \qquad (6)$$

$$[C_6H_5CHCN]Na + 2H \longrightarrow C_6H_5CH_3 + NaCN \qquad (7)$$

This result agrees with the observations of E. von Meyer and his collaborators.[6] However, these earlier investigators obtained a salt of formula $C_{16}H_{13}N_2Na$, the salt of a condensation product rather than of the nitrile itself. Condensations (of the aldol type) probably occur in this series, exactly as in the formation of acetoacetic ester from ethyl acetate. The formation of hydrogen as a by-product of the reaction, as expressed in Equation 6, and the consequent partial reduction of sodium phenylacetonitrile to toluene and sodium cyanide (Equation 7) is highly undesirable from the point of view of yield of the salt. Since this salt and others of its kind are exceedingly important compounds, not only for their theoretical interest but as preparative reagents, it is of vital importance to develop methods of preparation in which the yield of the salts is not diminished by their reduction. Methods of this sort have been studied by Rising and collaborators,[7] in which sodamide and sodium ethylate are used to produce the salts rather than metallic sodium. Success has attended these efforts and excellent yields of the pure salts have been obtained in the case of a number of nitriles. These results will be published in due time.

Experimental Part

The Course of the Reaction of Sodium with **Phenylacetonitrile.** The Isolation of Pure Sodium Phenylacetonitrile, $[C_6H_5CH{=}C{=}N^-]Na^+$ and $[C_6H_5C^-HCN]Na^+$.

1. Apparatus and Reagents.—Reactions were carried out in Apparatus I (diagram). Apparatus II consists of Apparatus I to which an apparatus for filtration in an atmosphere of nitrogen is added. Before use all apparatus was freed from air and moisture by passage through it of a stream of dry oxygen-free nitrogen for two hours, while Flask A was warmed. All reactions were carried out in an atmosphere of pure nitrogen.

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[6] Wache, *J. prakt. Chem.*, 39, 245 (1889); von Meyer, *ibid.*, 52, 114 (1895), etc.

[7] Work on these problems is being continued by M. M. Rising with the coöperation of E. W. Lowe, C. M. Marberg and K. T. Swartz.

Eastman's best phenylacetonitrile was used, after two fractionations, the product showing a freezing point of −24° and n? **1.5242.**

2. Procedure. Preparation of the Salt.—When Apparatus I is ready for use, freshly cut sodium (**13.0** g.), used in 15% of the calculated amount (Equation **7**), is introduced into Flask A under dry xylene and powdered in the usual way. The xylene is then replaced by **250** cc. of ether, and nitrogen is led through the apparatus for three hours. The ether is then boiled for fifteen minutes and phenylacetonitrile (**58.5 g.**), in a 50% ethereal solution, is added from the dropping funnel during forty-five minutes, the reaction mixture being kept boiling and being vigorously stirred. The sodium dissolves, a precipitate appears and the solution becomes yellow. After the addition of the nitrile the reaction mixture is boiled for two hours, and the reaction is then complete. During the entire operation and during the filtration of the solution, nitrogen is led through the apparatus. Stirring can be carried out in such a way that the unused sodium collects in a mass.

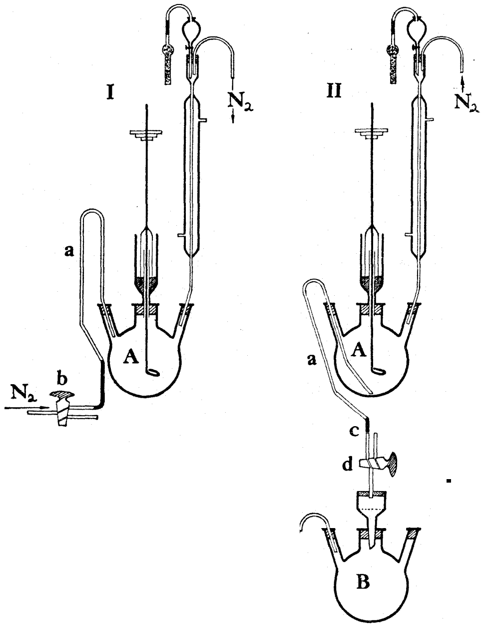

Fig. **1.**

Filtration.—When the reaction just described is complete, the precipitate is allowed to settle. Siphon a is now attached by means of the rubber connection on Tube c to Flask B, which carries a filter funnel closed with a rubber stopper. This stopper holds a three-way stopcock, d. The direction of the nitrogen stream is now reversed, so that the gas enters the apparatus at the top of the condenser and leaves through a side arm of Flask B. The apparatus is evacuated, Siphon a is lowered into the clear solution in Flask A and filtration is started by opening Stopcock d. When the supernatant liquid is removed, Siphon a is lowered to the bottom of Flask A; the precipitate is drawn upon the filter and washed with ether introduced through the dropping funnel. The unused sodium remains in Flask A, the precipitate on the filter is sodium cyanide, and Filtrate F contains sodium phenylacetonitrile and toluene.

3. Quantitative Determination of the Course of the Reaction.—This was accomplished by determining **(1)** the amount of sodium left unused, **(2)** the amount of sodium cyanide formed and **(3)** the amount of sodium phenylacetonitrile produced.

(1) Unused Sodium.—The **15%** excess of sodium, used to bring the reaction to completion, remained in Flask A. It was dissolved in alcohol and the alcoholic solution titrated in the usual way. In four preparations of the salt, in each of which **13.0 g.** of sodium and **58.5** g. of nitrile were used, **1.4** g. of sodium remained unused (Equation **5**). The theoretical amount of sodium was therefore consumed in the reaction.

(2) Sodium Cyanide.—The light colored precipitate formed in the reaction mixture, in quantity **13–14** g., proved to be nearly pure sodium cyanide.

Anal. Subs., **0.4100, 0.3322** (from two different preparations): Na_2SO_4, **0.5449, 0.4755.** Calcd. for NaCN: Na, 46.97. Pound: Na, **43.00, 41.50.**

The amount of sodium cyanide so obtained in a given preparation was determined by titration with silver nitrate. From 13.09 g. of sodium and 58.5 g. of nitrile, 11.7 g. of sodium cyanide was produced, corresponding to 5.49 g. of sodium, and to 95.3% of the amount of cyanide which could be formed from phenylacetonitrile and sodium (Equation 5). In similar experiments an average of 11.88 g. of cyanide was formed, corresponding to 50% of the nitrile used.

(3) Sodium Phenylacetonitrile.—Filtrate F was investigated (a) to determine the amount of sodium phenylacetonitrile formed and so account for the rest of the sodium used and (b) to isolate the salt for analysis.

(a) Quantitative Determination of the Salt.—This was accomplished in two ways: by ethylation of the salt in Filtrate F, a nearly quantitative yield of α-phenylbutyronitrile being so obtained, and by conversion of the salt into phenylacetonitrile in nearly quantitative yield by treatment with acid.

Ethylation.—For the ethylation of the salt, Flask B, containing Filtrate F, was put in place of Flask A and 50 g. of ethyl iodide was introduced with vigorous stirring during twenty minutes (nitrogen atmosphere). The reaction mixture was then heated for an hour and to it was added ligroin (b. p. 30–50°) to precipitate the sodium iodide formed in the alkylation. The iodide was collected and its purity determined by titration with silver nitrate. The total amount of iodide produced was found to be 34.8 g., corresponding to 5.34 g. of sodium. The α-phenylbutyronitrile was separated from the reaction mixture by fractional distillation, Fraction I boiled up to 110° at 15 mm., weighed 9 g. and had the odor of toluene. Of this 4 g. boiled at 105–108° and 4 g. at 108–110' at atmospheric pressure, the fraction of b. p. 108–110' showing n_{D}^{20} 1.4960 (pure toluene n_{D}^{20} 1.49552). The residue from the crude toluene boiled at 122° at 15 mm., the distillate showing n_{D}^{20} 1.5097 (pure α-phenylbutyronitrile n_{D}^{20} 1.5092). The amount obtained was 31.7 g., a 94% yield of the nitrile calculated on the basis of the sodium in the ethereal solution (5.34 g. of sodium in the sodium iodide formed).

The quantitative study of the reaction has shown that of the 13.0 g. of sodium used to react with 58.5 g. of nitrile, 5.34 g. was converted into sodium phenylacetonitrile, 5.49 g. into sodium cyanide and 1.4 g. was unused. We have therefore accounted for 12.32 g. of the sodium used, or 95% (5% loss in operations, etc.).

(b) Treatment of Sodium Phenylacetonitrile with Acid.—A filtrate, F, containing the salt obtained by treatment of 58.5 g. of phenylacetonitrile with 13.0 g. of sodium, was treated with a small excess over the calculated amount of dilute sulfuric acid, while being stirred and kept cold. The ether layer which separated was removed, washed and dried. After evaporation of the ether, a residue of oil yielded on distillation under reduced pressure a fraction boiling up to 110° at 16 mm. This distillate weighed 8.0 g. and contained toluene. The main fraction of distillate, 25.2 g., boiled at 112–113° at 16 mm. and showed n_{D}^{20} 1.5242 (pure phenylacetonitrile n_{D}^{20} 1.5242).

4. Reduction of Sodium Phenylacetonitrile by Hydrogen.—A filtrate, F, obtained from 58.5 g. of nitrile and 13.0 g. of sodium in the way described, was refluxed for three hours with 13.0 g. of sodium powder and 75 cc. of absolute alcohol, the mixture being stirred. After removal of excess sodium, the reaction mass was dissolved in water and this solution was extracted with ether. When the ether extract had been dried and the ether removed, the oil which remained yielded on distillation 10 g. of pure toluene, n_{D}^{20} 1.4958 (pure toluene n_{D}^{20} 1.49552). The aqueous solution was found by the Volhard method to contain 8.2 g. of sodium cyanide, or 75% of the amount obtainable according to Equation 7.

5. Isolation of Sodium Phenylacetonitrile.—The reaction mixture obtained by treatment of 25.0 g. of phenylacetonitrile with 5.05 g. of sodium in the way described was filtered into 1.8 liters of ligroin (b. p. 30–50°) in a stream of nitrogen. A light yellow

salt precipitated in large quantity. A suspension of the salt in ligroin was transferred to a weighed flask and the ligroin was removed at reduced pressure in a nitrogen atmosphere. Sodium phenylacetonitrile remained in the weighing bottle.

Anal. Subs., 0.4706, 0.6150 (from two different preparations):[8] Na_2SO_4, 0.2295, 0.2995. Calcd. for NaC_8H_6N: Na, 16.53. Found: Na, 15.79, 15.76.

Properties of Sodium Phenylacetonitrile. 1. Physical.—The salt is a light yellow amorphous powder as precipitated from ether by ligroin at room temperature. A 10% ether solution of the salt cooled to −80° slowly deposits large crystals. The salt is very soluble in ether and in phenylacetonitrile; it is insoluble in ligroin.

2. Chemical.—The salt turns brown immediately upon exposure to air, then smokes, collapses, glows and turns to a tar which hardens on cooling. The products of this decomposition are being studied. When the salt is precipitated with ligroin, a slow decomposition into sodium cyanide occurs. Not all of the salt so precipitated can be redissolved in ether and the insoluble residue contains sodium cyanide. The same change occurs after redissolving and reprecipitating the salt. Treatment of the salt with acid converts it into phenylacetonitrile. Reduction of sodium phenylacetonitrile with hydrogen was found to produce toluene and sodium cyanide. Hence it is to be concluded that the hydrogen formed when phenylacetonitrile is treated with sodium (Equation 6) reduces part of the sodium salt, under the conditions used by Braun (and von Meyer).

Summary

1. The von Meyer reaction of phenylacetonitrile with sodium has been studied quantitatively and the exact course of the reaction established.

2. A satisfactory method for the preparation and isolation of pure sodium phenylacetonitrile has been developed and used with excellent results by a number of workers.

3. The reducing action of hydrogen formed in the reaction of sodium with phenylacetonitrile has been found to account for the failure to obtain sodium phenylacetonitrile in quantitative yield.

CHICAGO, ILLINOIS

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[8] The first of the two sets of data was obtained by C. M. Marberg, who prepared the salt by the Braun method.

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

THE RAPID DETERMINATION OF SULFUR IN ORGANIC COMPOUNDS[1]

BY E. WERTHEIM

RECEIVED SEPTEMBER 6, 1929 PUBLISHED MARCH 6, 1930

With the exception of certain special cases the determination of sulfur in an organic compound involves (1) oxidation of sulfur to sulfate and (2) determination of sulfate ion. The Carius method and numerous methods which depend upon fusions in open vessels are still in use for the oxidation of sulfur compounds, but are open to objection in that either they are too complicated and time consuming or they are not universally applicable.

These objections can hardly be urged against the fusion method devised by Parr;[2] because of its great rapidity and simplicity this method should be more generally used than seems to be the rule at present. The Parr method was employed in the work described herein.[3]

The estimation of sulfate ion is ordinarily accomplished by the precipitation and weighing of barium sulfate. Accurate results may be obtained but the procedure is necessarily slow. It was considered desirable to supplant this with a volumetric method which would give as accurate results in much less time. A survey of the literature discloses several reliable volumetric methods, the simplest in principle and procedure being the method of Wildenstein.[4]

In this method a solution containing sulfate is titrated with a slight excess of barium chloride solution, the excess being determined with potassium chromate which is added until a yellow color is noted. A solution of a lead salt is used as external indicator when such is necessary. It was found on trial that this method could be applied but only with considerable difficulty.

The method has been modified so as to use ferrous thiocyanate as an external indicator. After removal of carbon dioxide and hydrogen peroxide from the solution as obtained from the bomb, chromate is added until tests with the ferrous thiocyanate indicator match the "standard end-point" hereinafter described. The barium sulfate is then precipitated, after which chromate is again added until tests match the standard end-

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Paper No. 170, Journal Series, University of Arkansas.

[2] Parr, THIS JOURNAL, 30, 764 (1908).

[3] For details of the method consult the Burgess-Parr Co., Moline, Ill. Cf. also Noyes, "Organic Chemistry for the Laboratory," Chemical Publishing Co., Easton, Pa., 1926, p. 28.

[4] Wildenstein, *Z. anal. Chem.*, 1, 323 (1862); Sutton, "Volumetric Analysis," Blakiston, 1924, p. 337 (modification); Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 1927, Vol. I, p. 505 (modification). For discussion of the method see Kolthoff, "Volumetric Analysis," John Wiley and Sons, Inc., New York, 1929, Vol. II, p. 418.

point. With this procedure the end-point is quickly and easily attained. The color at the end-point is very easy to match and the indicator is sufficiently sensitive to show a noticeable change of color upon the addition of 2 or **3** drops of chromate solution to a volume of 200 cc. It is neither necessary to wait for complete settling of the precipitate while adjusting the end-point, nor to repeatedly boil the solution during the analysis as in the Wildenstein procedure.

Procedure

The solution and washings from the bomb are collected in a 600-cc. beaker. A few chips of porous plate are added, the beaker is covered and the contents boiled for fifteen minutes. The solution is then treated with **3** or 4 drops of dilute phenolphthalein solution.[5] Concentrated hydrochloric acid is added until the reaction is distinctly acid. The solution is filtered[6] if necessary, then chromate solution is added from the buret until a slight yellow color is noted; about 10 drops will suffice. The solution is maintained at a temperature of 80–90° for about ten minutes, then allowed to cool to 70–80° and treated with dilute sodium hydroxide solution until a faint pink color is reached. Slight changes in P_H during the titration will not notably affect the end-point; however, it is well not to add an excess of base. The indicator solution is prepared from potassium thiocyanate, 1.0 g., ferrous sulfate, 1.5 g., water, 50 cc., dilute (1:1) hydrochloric acid, 15 drops. If the solution is colored the color is discharged by the addition of sodium hyposulfite ($Na_2S_2O_4$).[7] About 0.010 g. will be required; an excess should be avoided. A testing solution is prepared from 100 cc. of water plus 10 drops of the standard chromate solution. The "standard end-point" is prepared by adding 4 drops of the testing solution to 2 drops of the indicator on a porcelain testing plate.

The solution being analyzed is now treated with chromate solution until the addition of 4 drops to *2* drops of indicator on the testing plate gives a color matching that of the standard end-point. This result is quickly attained, usually taking but a few moments.[8] Tests are best made from a pipet fitted with a rubber bulb ("medicine dropper" type). When the end-point is satisfactorily adjusted, the solution is held for five minutes and again tested at approximately the same temperature as before (70–80°). In the majority of cases there is no change, all peroxide having been removed by previous treatment. Twenty drops of 1:1 hydrochloric acid are added, after which the calculated amount of barium chloride solution plus an excess of **1** or *2* cc. is delivered from the buret. **A** large excess of barium solution should be avoided as it will delay the attainment of the final end-point.[9]

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[5] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1911, Vol. I, p. 35.

[6] The total volume at this point should not exceed 200 cc.

[7] The indicator will remain colorless for three or four days if not placed in direct daylight. It may be "revived" several times with sodium hyposulfite without loss of sensitivity.

[8] If by error too much chromate solution is used the excess is removed by the addition of hydroxylamine hydrochloride solution (1/2%) drop for drop against the excess chromate. After standing for a few minutes the titration may proceed.

[9] When the percentage of sulfur in the compound is not known, the acidification noted above is omitted. Barium solution is added a few cc. at a time, the solution being set aside for about two minutes after each addition and a thorough stirring. When an excess of barium solution has been added the indicator will give no color. The solution is now acidified and the analysis completed in the usual way.

The solution is gently boiled for five minutes, cooled to 70–80° and neutralized with sodium hydroxide as before. Chromate solution is added until the end-point secured will match the standard end-point. After five minutes the solution is again tested. Ordinarily another small addition of chromate will be needed. After standing for another five minutes the end-point is usually unchanged. The solution is now acidified with 2 drops of 1:1 hydrochloric acid, held for five minutes at 80–90° and again neutralized with sodium hydroxide solution. In most cases the end-point will be unchanged by this treatment but in an analysis requiring a large amount of barium solution a little more chromate may be needed. With practice it will become unnecessary to cool the solution; the temperatures have been so chosen that with several analyses on hand the solutions will cool to the proper point during the various manipulations without extra attention. The complete analysis takes about one and one-half hours.

Preliminary Tests of the Method.—The $N/20$ barium chloride solution was standardized by weighing as barium sulfate. Expressed as mg. of sulfur per cc. of solution the average of five concordant results was 1.6360. The $N/20$ potassium chromate solution was standardized by weighing as barium chromate. Expressed as mg. of sulfur per cc. of solution the average of four concordant results was 1.602.

The ratio of the two solutions above was taken in 200 cc. of water, using the same technique as described above for analysis. The following ratios of potassium chromate-barium chloride were secured: 1.0228, 1.0214, 1.0223, 1.0207, 1.0226, 1.0254; average, 1.0226. Making use of the above ratio and the measured value of the chromate solution, calculation assigns to the barium chloride solution 1.6383 mg. sulfur per cc. The value actually found was 1.6360.

Lastly a sample of C. P. potassium sulfate was analyzed for sulfur by the precipitation and weighing of barium sulfate, giving the following values: 18.19, 18.19%. Analysis by the volumetric method gave: 18.22, 18.28%.

Results

The following table presents the results obtained in the analysis of several organic compounds by the volumetric method. As a check these compounds were also analyzed by the ordinary gravimetric procedure

TABLE I

ANALYSIS OF ORGANIC SULFUR COMPOUNDS

	Percentage of sulfur			
Compound	**Caled.**	**Volumetric method**	**Gravimetric check**	**Gravimetric method**
o-Chlorobenzenesulfonamide	16.74	16.64, 16.73	16.40, 16.73	16.71
n-Butyl sulfone	17.99	18.11, 18.03	17.46, 17.48[a]	17.46, 17.80
Diphenyl sulfone	14.69	14.62, 14.52	15.05	14.54
Benzyl sulfide	14 98	14.98, 14 82	14 89[a]	14.83
Diphenyl sulfoxide	15.86	15.60, 15.66	16.10 (av.), 15.69"	15.73
Sulfonal	28.10	28.02, 27.90	27.96"	27.78
Di-p-tolyl sulfone	13.01	12.95, 12 89 12.98, 12.96	13 30	12.97
o-Benzoic sulfinide	17.52	17.47, 17.80		17.45
Allyl thiourea (crude)	27.63	26.43, 26.20	26.27"	26.53
N-Benzoylbenzenesulfonamide	12.28	12.26, 12.22 12.07	12.04[b]	12.22

[a] Precipitate digested with dilute nitric acid.

[b] Precipitate digested with oxalic acid.

following their oxidation in the Parr bomb. The gravimetric results are shown in Col. 5. Column 4 marked "Gravimetric check" presents results obtained as follows: immediately at the close of the volumetric analysis the solution was treated with 2 cc. of 1:1 hydrochloric acid and heated to boiling. Twenty-five cc. of hydrogen peroxide (3%) was added to the boiling solution. After the customary period allowed for digestion, the precipitate of barium sulfate was collected and weighed in the usual manner. Not all of the barium chromate is removed by this procedure; enough usually remains to give the precipitate an *extremely faint* yellow tint. However, the results show a fair agreement with those of the direct analysis and in some cases may prove of value as a check.

Summary

The Wildenstein volumetric method of analysis for sulfate has been modified by the use of ferrous thiocyanate as an external indicator and adapted to the analysis of organic compounds following their oxidation in the Parr bomb. Provision has been made for a gravimetric check upon the volumetric procedure.

FAYETTEVILLE, ARKANSAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

O-ALKYL SUBSTITUTED HYDROXYLAMINO ACIDS, ESTERS AND ALCOHOLS[1]

BY LAUDER W. JONES AND RANDOLPH T. MAJOR

RECEIVED SEPTEMBER 14, 1929 PUBLISHED MARCH 6, 1930

N-Hydroxylamino acids of the type, $HONHC_nH_{2n}COOH$, have been prepared,[2] as have also O-hydroxylamino acids of the type, $H_2NOC_nH_{2n}COOH$,[3] but no O-alkyl substituted hydroxylamino acids or esters with the general formula, $RONR'C_nH_{2n}COOR''$, in which R' and R'' may either be alkyl groups or .hydrogen, are described in the chemical literature. As a part of a general study of O-alkyl substituted hydroxylamines, it was thought that it would be of interest to synthesize a few substances of this type and to investigate their properties, especially since they would be derivatives of that very important class of chemical compounds, the amino acids.

When ethyl bromo-acetate was treated with two molecular equivalents of O,N-dimethylhydroxylamine, there was formed ethyl methylmethoxy-

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

[2] Traube, *Ber.*, 28, 2298 (1895); Gomberg, Ann., 300, 75 (1898); Hantzsch and Wild, *ibid.*, 289, 309 (1896).

[3] Werner, *Ber.*, 26, 1567 (1893); Werner and Sonnenfeld, *ibid.*, 27, 3350 (1894); Werner and Bial, ibid., 28, 1378 (1895); Werner and Falck, *ibid.*, 29, 2658 (1896).

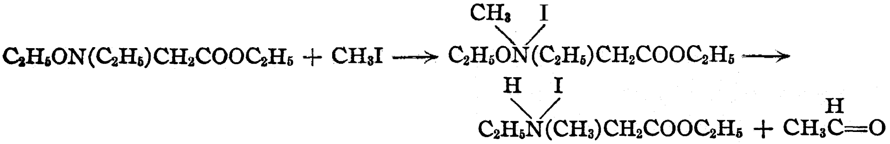
amino-acetate and O,N-dimethylhydroxylammonium bromide, according to the equation

$$2CH_3ONHCH_3 + BrCH_2COOC_2H_5 \longrightarrow CH_3ON(CH_3)CH_2COOC_2H_5 + CH_3O\overset{H}{N}CH_3\cdot HBr$$

Ethyl methylmethoxyamino-acetate was a liquid which rather closely resembled in properties the amino ester to which it is most closely related, ethyl dimethylamino-acetate, $(CH_3)_2NCH_2COOC_2H_5$. That O-alkyl substituted hydroxylamines, in general, have properties often closely resembling those of the alkyl substituted amines to which they are related may readily be seen by comparing their respective properties. This similarity has been pointed out by Jones and Major in connection with a study of the physiological properties of certain O-alkyl substituted hydroxylamines.[4] The boiling points of the derivatives of hydroxylamine are, however, in general somewhat higher than those of corresponding derivatives of ammonia.

When ethyl bromo-acetate was treated with O,N-diethylhydroxylamine, there was formed ethyl ethylethoxyamino-acetate, $C_2H_5O(C_2H_5)NCH_2COOC_2H_5$. It was thought that methyl iodide would react with this compound to form a methiodide. Instead, however, there were formed acetaldehyde and ethyl methylethylamino-acetate hydroiodide. The hydrochloride of the latter substance was synthesized by adding hydrogen chloride to the ether-soluble oil formed by the interaction of ethyl bromo-acetate and methylethylamine.

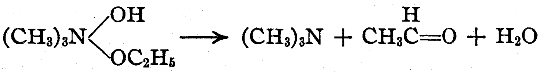
It seems probable that the formation of acetaldehyde and ethyl methylethylamino-acetate hydroiodide from methyl iodide and ethyl ethylethoxyamino-acetate involved the intermediate formation of ethyl ethylethoxyamino-acetate methiodide, which was so unstable that it decomposed almost as soon as it formed. This may be represented by the equations



$$C_2H_5ON(C_2H_5)CH_2COOC_2H_5 + CH_3I \longrightarrow C_2H_5O\overset{CH_3\quad I}{N}(C_2H_5)CH_2COOC_2H_5 \longrightarrow$$

$$C_2H_5\overset{H\quad I}{N}(CH_3)CH_2COOC_2H_5 + CH_3\overset{H}{C}{=}O$$

Meisenheimer has shown that trimethylethoxyammonium hydroxide decomposes in a somewhat similar manner into trimethylamine, water and acetaldehyde[5]



$$(CH_3)_3N\genfrac{}{}{0pt}{}{OH}{OC_2H_5} \longrightarrow (CH_3)_3N + CH_3\overset{H}{C}{=}O + H_2O$$

By the action of O-methylhydroxylamine on ethyl bromo-acetate, there has been obtained O-methylhydroxylammonium bromide and ethyl methoxyamino-acetate, $CH_3ONHCH_2COOC_2H_5$, which may be considered

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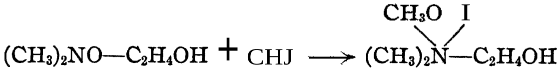
[4] Jones and Major, This Journal, 49, 1540 (1927).

[5] Meisenheimer, *Ann.*, 397, 294 (1913).

an hydroxylamine analog of the important amino acid sarcosine, $CH_3NHCH_2COOC_2H_5$. Potassium cyanate with ethyl methoxyamino-acetate hydrochloride formed ethyl N-methoxyhydantoate, $H_2NCON(OCH_3)CH_2COOC_2H_5$. When a solution of this ester in concentrated hydrochloric acid was evaporated to dryness, the corresponding acid, N-methoxyhydantoic acid, was obtained. With phenyl isocyanate and phenyl isothiocyanate the expected derivatives were obtained.

It was thought that the hydroxylammonium analogs of choline and its salts, namely, dimethylmethoxyhydroxyethylammonium hydroxide and its salts, might perhaps be prepared, as shown by the two equations

$$(CH_3)_2NC_2H_4OH + H_2O_2 \longrightarrow (CH_3)_2NOC_2H_4OH + H_2O \qquad \text{(I)}$$



$$(CH_3)_2NO—C_2H_4OH + CH_3I \longrightarrow (CH_3)_2\overset{CH_3O\ \ I}{\overset{\diagdown\,\diagup}{N}}—C_2H_4OH \qquad \text{(II)}$$

The amine oxide of dimethylamino-ethanol was obtained by the action of hydrogen peroxide on dimethylamino-ethanol, as shown in Equation I, and several salts of this compound, as well as the picrate of diethylhydroxyethylamine oxide, were made. However, we were not able to isolate dimethylmethoxyhydroxyethylammonium iodide from the products of interaction of dimethylhydroxyethylamine oxide and methyl iodide.

When the attempt was made to repeat the preparation of dimethylmethoxyhydroxyethylammonium iodide according to the method of Jones and Major,[6] it was found that in order to obtain the intermediate compound, O,N-dimethyl-N-hydroxyethylhydroxylamine, $CH_3O(CH_3)NC_2H_4OH$, which also was described by Jones and Major,[6] it was necessary to add a trace of moisture to the mixture of ethylene oxide and O,N-dimethylhydroxylamine from which the compound was made and that the compound was not obtained under the conditions described by Jones and Major if moisture was not present. It was also found that any more than a trace of moisture caused the reaction to proceed in such a way that no O,N-dimethyl-N-hydroxyethylhydroxylamine but only higher-boiling oils were obtained. Similarly, the presence of a trace of moisture was found to be essential in the preparation of O,N-diethyl-N-hydroxyethylhydroxylamine, according to the method of Jones and Burns.[7] Presumably, the required moisture was accidentally introduced during the earlier experiments with these compounds.

When dimethylmethoxyhydroxyethylammonium hydroxide, $(CH_3)_2(CH_3O)N(OH)C_2H_4OH$, was previously decomposed by us, by heating it, the analyses did not absolutely prove that formaldehyde and dimethylamino-ethanol were obtained.[6] Both of these compounds have now been identified definitely as the products which are formed in the decomposition of this substance.

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[6] Jones and Major. **This Journal**, 49,1533 **(1927).**

[7] Jones and **Burns**, *ibid.*, 47, **2972 (1925).**

Experimental Part

Reaction of Ethyl Bromo-acetate with O,N-Dimethylhydroxylamine.—After a solution of 0.1 mole of ethyl bromo-acetate and 0.2 mole of O,N-dimethylhydroxylamine in dry ether had stood at room temperature for two days, a precipitate of white, crystalline needles had formed. These crystals were filtered, dissolved in absolute alcohol and then reprecipitated with dry ether; m. p. 143°. They gave a test for the bromide ion with silver nitrate. In order to identify this compound it was treated with potassium hydroxide and the free base which was thus formed was distilled into dilute hydrochloric acid. The hydrochloric acid solution was evaporated to dryness on a water-bath. The solid which remained melted at 115–116° and a mixture of this substance with O,N-dimethylhydroxylammonium chloride, m. p. 115–116°, also melted at this temperature, indicating that the bromide which melted at 143° was O,N-dimethylhydroxylammonium bromide.

Anal. Subs., 0.2407: AgBr, 0.3192. Calcd. for C_2H_8ONBr: Br, 56.28. Pound: Br, 56.40.

Dry hydrogen chloride gas was passed into the ether filtrate from which the above described O,N-dimethylhydroxylammonium bromide was filtered. The white solid which formed was dissolved in water. This solution was made basic with alkali and then repeatedly extracted with ether. The ether solution was dried with anhydrous sodium sulfate, after which the ether was distilled off. A colorless oil remained; b. p. 164–166"; yield of ethyl methylmethoxyamino-acetate, 20%. The oil was rather soluble in water but more so in ether.

Hydrochloride of Ethyl Methylmethoxyamino-acetate, $CH_3O(CH_3)NCH_2COOC_2H_5\cdot HCl$.—The hydrochloride of the above described oil, b. p. 164–166°, was a white solid. It was recrystallized by dissolving it in alcohol and reprecipitating it with ether; m. p. 90–91°.

Anal. Subs., 0.2033: AgCl, 0.1602. Calcd. for $C_6H_{14}O_3NCl$: Cl, 19.32. Found: 19.52.

Reaction of O,N-Diethylhydroxylamine with Ethyl Bromo-acetate.—After a solution of 0.02 mole of ethyl bromo-acetate and 0.04 mole of O,N-diethylhydroxylamine in dry ether had stood at room temperature for four days, an oily liquid had precipitated. It was separated by decantation from the ether solution and was washed with ether. It did not solidify when it was allowed to stand for several days in a vacuum desiccator with concentrated sulfuric acid and potassium hydroxide. Accordingly, it was treated with potassium hydroxide and the free base distilled. The base possessed the characteristic odor of O,N-diethylhydroxylamine and boiled at 83°.[8]

Hydrogen chloride caused a heavy pale yellow oil to precipitate from the ether solution from which the above described O,N-diethylhydroxylammonium bromide was separated. It was separated from the ether solution by decantation and washed with ether. Since the oily hydrochloride appeared to be an extremely weak base and was somewhat soluble in ether which contained no hydrogen chloride, the ether solution in addition was extracted with dilute hydrochloric acid and this acid solution added to the oily hydrochloride. After fresh ether had been added to this hydrochloric acid solution in order to dissolve any free base as soon as it formed, the aqueous solution was made basic with solid sodium carbonate and some caustic alkali. The ether layer was separated and the aqueous solution repeatedly extracted with further portions of ether. The combined ether extracts were dried with anhydrous sodium sulfate. After the ether had been removed by distillation, an oil remained which was purified by distillation; b. p. 186–188° with slight decomposition, and 82° at 19 mm. It had a rather

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[8] Lossen, Ann., 252, 234 (1889), gives 83° as the b. p. of O,N-diethylhydroxylamine.

pleasant ethereal odor. It formed neither a solid hydrochloride nor chloroplatinate; yield of ethyl ethylethoxyamino-acetate, 43%.

Anal. Subs., 0.3643: N_2, 26.8 cc. (21°, 754 mm.). Calcd. for $C_8H_{17}O_3N$: N, 8.00. Found: N, 8.45.

Ethyl **Methylethylamino-acetate,** $C_2H_5(CH_3)NCH_2COOC_2H_5$.—To a cooled solution of 0.07 mole of methylethylamine in dry ether was slowly added a solution of 0.07 of a mole of ethyl bromo-acetate in ether. There was a vigorous reaction which was accompanied by considerable heat. A white solid precipitated, m. p. 85–88°, which was apparently methylethylammonium bromide.[9] Ethyl methylethylamino-acetate was recovered from the ether filtrate in the same way that has already been described for the preparation of ethyl methylmethoxyamino-acetate. It was an oily liquid, b. p. 164–165°.

Hydrochloride.—The hydrochloride was precipitated from ether in the usual manner, m. p. 132°.

Anal. Subs., 0.2720: AgCl, 0.2142. Calcd. for $C_7H_{16}O_2NCl$: Cl, 19.53. Found: Cl, 19.50.

Reaction of Methyl Iodide with Ethyl Ethylethoxyamino-acetate.—To 1 g. of ethyl ethylethoxyamino-acetate was added a molecular equivalent of methyl iodide. The mixture was allowed to stand in a sealed container at room temperature for two weeks. During this time a heavy reddish oil formed. the amount of which gradually increased until at the end of two weeks the reaction was apparently complete. When the container was opened the odor of acetaldehyde was quite pronounced. Accordingly the heavy oil was repeatedly extracted with ether in order to remove the acetaldehyde. The ether extract was shaken with an aqueous solution of *p*-nitrophenylhydrazine hydrochloride until there was no further reaction. The ether was then evaporated. A yellow precipitate remained which was recrystallized from 50% alcohol; m. p. 129°. A mixture of this solid with pure acetaldehyde *p*-nitrophenylhydrazone, m. p. 129°, also melted at 129°. There was obtained 0.24 g. of acetaldehyde *p*-nitrophenylhydrazone in this way. This means that 21% of the theoretical amount of acetaldehyde was recovered in this process if it is assumed that all of the ethoxy group present in the ethyl ethylethoxyamino-acetate was converted into acetaldehyde. That some of the acetaldehyde polymerized during the reaction and therefore was not recovered by this process seems very probable. Also, the ether probably did not completely extract the acetaldehyde from the oil.

The pink oil was then dissolved in absolute alcohol and shaken with metallic mercury, in order to remove free iodine. It was then shaken with somewhat more than the calculated amount of silver chloride until its solution no longer gave a test for iodide ion. Dry ether was then added to the alcoholic filtrate from this reaction and a heavy almost colorless oil precipitated. This oil was allowed to stand in a vacuum desiccator with sulfuric acid for some time but did not solidify. It was then redissolved in warm absolute alcohol and fractionally precipitated with dry ether. The first fractions were oils which were not identified. A rather larger solid precipitate then formed as more ether was added. In order to purify it, it was dissolved in alcohol, shaken with animal charcoal, filtered and reprecipitated with ether; m. p. 132°. A mixture of this hydrochloride with pure ethyl methylethylamino-acetate hydrochloride, m. p. 132°, also melted at 132°.

Reaction of O-Methylhydroxylamine with Ethyl Bromo-acetate.—After a solution of 0.1 mole of ethyl bromo-acetate and 0.2 mole of O-methylhydroxylamine in dry ether

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[9] Wagner, *Z. Krist.*, 43, 162 (1907), gives 85–88° as the m. p. of methylethylammonium bromide.

had stood at room temperature for five days, the white plate-like crystals which had formed were removed by filtration. They were purified by dissolving in absolute alcohol and precipitating with dry ether; m. p. 164° with decomposition; yield, 63%.

Anal. Subs., 0.2251: AgBr, 0.3325. Calcd. for $CH_3ONH_2\cdot HBr$: Br, 62.45. Found: Br, 62.86.

Ethyl methoxyamino-acetate, $CH_3ONHCH_2COOC_2H_5$, was recovered from the ether filtrate in the same manner that has already been described for the preparation of ethyl methylmethoxyamino-acetate; b. p. 167–170° (with some decomposition), 112° at 116 mm.; yield, 23%.

Chloroplatinate of Ethyl Methoxyamino-acetate, $(CH_3ONHCH_2COOC_2H_5)_2\cdot H_2PtCl_6$.—An equivalent of dry hydrogen chloride was passed into a solution of 0.5 g. of ethyl methoxyamino-acetate in absolute alcohol. To this was added the calculated amount of a concentrated solution of chloroplatinic acid in absolute alcohol. The orange colored crystals which precipitated were recrystallized by dissolving in absolute alcohol and reprecipitating with ether; m. p. 141° with decomposition.

Anal. Subs., 0.1998: Pt, 0.0571. Calcd. for $C_{10}H_{24}O_6N_2\cdot PtCl_6$: Pt, 28.87. Found: Pt, 28.58.

Ethyl **N-Methoxyhydantoate**, $NH_2—CO—N(OCH_3)CH_2COOC_2H_5$.—A solution of 2 g. of ethyl methoxyamino-acetate in dry ether was saturated with dry hydrogen chloride, The oil which precipitated was separated and washed with ether. A cold saturated solution of the calculated amount of potassium cyanate was slowly added to this hydrochloride while the reaction mixture was kept cold and stirred. Considerable heat developed and a white solid precipitated. It was filtered off, washed with a little water and recrystallized from absolute alcohol; m. p. 112°; yield, 65%. It was somewhat soluble in water, less so in methyl alcohol, still less so in ethyl alcohol and only very slightly soluble in ether.

Anal. Subs., 0.1740: N_2, 24.6 cc. (24°, 741.7 mm.). Calcd. for $C_6H_{12}O_4N_2$: N, 15.91. Found: N, 15.87.

N-Methoxyhydantoic Acid, $NH_2—CO—N(OCH_3)CH_2COOH$.—Slightly more than enough of a 37% solution of hydrogen chloride in water to dissolve it was added to 1 g. of ethyl N-methoxyamino-acetate. After the solution had stood at room temperature overnight, it was placed in a vacuum desiccator containing sulfuric acid and potassium hydroxide. Evaporation of the liquid left a white solid. It was recrystallized from absolute alcohol; decomposition point, 164°; yield, 70%. It was soluble in water and acetone, less so in alcohol, still less so in ether and insoluble in ligroin. It reacted quite acid to litmus and gave no test for the chloride ion with acid silver nitrate. However, when ammoniacal silver nitrate was added to an aqueous solution of the acid, its white silver salt precipitated.

Anal. Subs., 0.1549: N_2, 25.3 cc. (21°, 747.5 mm.). Calcd. for $C_4H_8O_4N_2$: N, 18.92. Found: N, 18.69.

Ethyl **N″-Phenyl-N′-methoxyhydantoate**, $C_6H_5NHCON(OCH_3)CH_2COOC_2H_5$.—To a solution of 0.5 g. of ethyl methoxyamino-acetate in dry ether was added 0.4 g. of phenyl isocyanate. After this mixture had stood overnight, petroleum ether was added. A precipitate of fine white needles formed which was recrystallized from hot ligroin; m. p. 91°. The crystals were very soluble in benzene, alcohol and ether but insoluble in water.

Anal. Subs., 0.2044: N_2, 20.1 cc. (26°, 749.0 mm.). Calcd. for $C_{12}H_{16}O_4N_2$: N, 11.11. Found: N, 11.08.

Ethyl **N″-Phenyl-N′-methoxythiohydantoate**, $C_6H_5NHCS—N(OCH_3)CH_2COOC_2H_5$.—To a solution of 2.5 g. of ethyl methoxyamino-acetate in ligroin was added 2.6

g. of phenyl isothiocyanate. Some heat developed and a white precipitate formed. After the mixture had stood overnight, the white solid was filtered off. It was recrystallized from hot carbon tetrachloride; m. p. 110"; yield, 60%. It was readily soluble in benzene.

Anal. Subs., 0.2629: N_2, 24.2 cc. (26°, 762.3 mm.). Calcd. for $C_{12}H_{16}O_3N_2S$: N, 10.45. Found: N, 10.55.

Dimethylhydroxyethylamine Oxide, $(CH_3)_2NOC_2H_4OH$.—To 10 g. of dimethylamino-ethanol an excess of a 3% solution of commercial hydrogen peroxide was added.[10] Considerable heat was generated in the reaction. After the solution had stood for twenty-five hours, platinum black was added in order to decompose the excess of hydrogen peroxide. The mixture was filtered and the excess of water was removed by distillation in *vacuo.* The oil which remained was thoroughly dried in a vacuum desiccator. In order to purify it, this oil was then dissolved in absolute alcohol, filtered and reprecipitated with dry ether. When the oil was further dried in a vacuum desiccator over phosphorus pentoxide, it solidified in the form of white, extremely hygroscopic crystals.

Hydrochloride.—A solution of dimethylhydroxyethylamine oxide in absolute alcohol was saturated with dry hydrogen chloride. An oil precipitated from this solution when ether was added, which solidified after it had stood for a short time. It was recrystallized by dissolving it in absolute alcohol and reprecipitating it with dry ether. It formed white, extremely hygroscopic crystals; m. p. 48–49°.

Anal. Subs., 0.1653: AgCl, 0.1705. Calcd. for $C_4H_{12}O_2NCl$: Cl, 25.06. Found: Cl, 25.45.

Chloroplatinate.—A solution of dimethylhydroxyethylamine oxide in absolute alcohol was saturated with dry hydrogen chloride. The calculated amount of chloroplatinic acid in absolute alcohol was added. An orange colored precipitate formed which was recrystallized from absolute methanol; it decomposed at 191°, with evolution of a gas.

Anal. Subs., 0.2349: Pt, 0.0733. Calcd. for $C_8H_{24}O_4N_2PtCl_6$: Pt, 31.48. Found: Pt, 31.21.

Picrate of Dialkylhydroxyethylamine Oxide.—The calculated amount of a concentrated solution of picric acid in absolute alcohol was added to a solution of the dialkylhydroxyethylamine oxide in absolute alcohol. Petroleum ether precipitated a yellow crystalline solid from this solution.

The picrate of dimethylhydroxyethylamine oxide was recrystallized from hot butanol. It formed long yellow needle-like crystals which were readily soluble in methyl and ethyl alcohols, acetone and water, much less soluble in chloroform, benzene and ether and insoluble in ligroin; m. p. 124".

Anal. Subs., 0.1793: N_2, 26.0 cc. (17°, 743.1 mm.). Calcd. for $C_{10}H_{14}O_9N_4$: N, 16.77. Found: N, 16.69.

The picrate of diethylhydroxyethylamine oxide was recrystallized from a solution of 75% of benzene and 25% of acetone. It formed yellow plate-like crystals which were soluble in acetone and alcohol, less so in ether and water and insoluble in petroleum ether; m. p. 125–126° with darkening.

Anal. Subs., 0.1773: N_2, 23.30 cc. (13°, 755.0 mm.). Calcd. for $C_{12}H_{18}O_9N_4$: N, 15.47. Found: N, 15.60.

Interaction of Dimethylhydroxyethylamine Oxide and Methyl Iodide.—The calcu-

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[10] The solution of hydrogen peroxide had been freed from sulfuric acid by shaking it with solid barium carbonate.

lated amount of methyl iodide was added to a solution of dimethylhydroxyethylamine oxide in absolute alcohol. After this solution had stood for four days dry ether was added. A heavy oil precipitated which readily dissolved in water. With silver nitrate it gave a precipitate of silver iodide. It was placed in a vacuum desiccator, but did not solidify. It was then fractionally precipitated from its solution in alcohol by the addition of dry ether. Each fraction was an oil which did not solidify, but which gave a precipitate of silver iodide with silver nitrate. No definite chemical compound was isolated.

Decomposition of Dimethylmethoxyhydroxyethylammonium Hydroxide.—To **0.5** g. of dimethylmethoxyhydroxyethylammonium iodide was added an excess of an aqueous solution of sodium hydroxide. The volatile portion of this solution was distilled into dilute hydrochloric acid. This acid solution was then found to give a positive test for formaldehyde with guaiacol sulfate.[11] The hydrochloric acid solution was evaporated to dryness on a water-bath. An oil was left which was dissolved in dry alcohol. The calculated amount of a solution of chloroplatinic acid in absolute alcohol was added to it. An orange colored precipitate formed, which was recrystallized from hot absolute alcohol; m. p. 178° with decomposition.

Anal. Subs., 0.0106: Pt, 0.0035. Calcd. for $((CH_3)_2NC_2H_4OH)_2 \cdot H_2PtCl_6$: Pt, 33.2. Found: Pt, 33.0.

The chloroplatinate of pure dimethylamino-ethanol was made in an analogous manner. It also melted with decomposition at 178° and exhibited the same properties of color and solubility that were shown by the chloroplatinate of the amine which was obtained in the decomposition of dimethylmethoxyhydroxyethylammonium hydroxide.

Summary

1. Two ethyl alkylalkoxyamino-acetates have been prepared by the action of O,N-dialkylhydroxylamines on ethyl bromo-acetate.

2. By the action of methyl iodide on ethyl ethylethoxyamino-acetate there was formed acetaldehyde and ethyl methylethylamino-acetate hydroiodide. The peculiar course of this reaction has been discussed.

3. Ethyl methoxyamino-acetate has been prepared by the action of O-methylhydroxylamine on ethyl bromo-acetate. Its reactions or those of its hydrochloride with potassium cyanate, phenyl isocyanate and phenyl isothiocyanate have been described.

4. N-Methoxyhydantoic acid has been obtained by hydrolyzing ethyl-N-methoxyhydantoate with hydrochloric acid.

5. Certain similarities in the properties of O-alkyl substituted hydroxylamines and the related amines have been pointed out.

6 Dimethylhydroxyethylamine oxide and several of its salts have been prepared.

7. Formaldehyde and dimethylamino-ethanol have been shown definitely to be formed in the decomposition of dimethylmethoxyhydroxyethylammonium hydroxide.

PRINCETON, NEW JERSEY

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[11] "Deutsches Arzneibuch," R. v. Deckers Verlag, Berlin, 1926, p. LIV

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

DETERMINATION OF SULFUR IN LIQUID ORGANIC COMPOUNDS[1]

BY E. WERTHEIM

RECEIVED SEPTEMBER 16, 1929 PUBLISHED MARCH 6, 1930

For the analysis of solid organic sulfur compounds various methods utilizing the Parr bomb have been developed which leave little to be desired and satisfactorily supplant the Carius method. In the case of compounds which are liquids at room temperature, this can hardly be claimed. Despite the various precautions which may be used the ignition of liquids is apt to be explosive and, in many instances, premature. For the analysis of such compounds another method of oxidation would be desirable.

The writer investigated the Klason method recently reported in a modified form by Leonard,[2] which seemed the simplest and most direct of the many reported methods. The initial intention was to modify the method so as to replace the expensive platinum catalyst by chromel. Chromel functioned about as well as platinum; however, it was soon found that the empty tube gave almost as good results as either chromel or platinum. This led to a modification in which chips of pyrex glass were substituted for the platinum catalyst. With this change the method becomes eminently satisfactory and there is no difficulty in procuring sufficient of the catalyst to insure complete oxidation of the sample.

One advantage of the Carius method is that several tubes may be run at one time. This has been offset by mounting two tubes side by side. Flashing during the analysis has been practically eliminated by the use of air instead of oxygen; it is, therefore, a simple matter to care for these two analyses simultaneously with good results. When the directions given by Leonard for the evaporation of the solution were followed literally high results were obtained. It was necessary to provide for more complete removal of the nitric acid before precipitating the barium sulfate.

Procedure

The illustration given in Leonard's article should be consulted. The bulb (E) contains about 50 cc. of fuming nitric acid.[3] The sample boat (D) is placed 8 cm. from the end of the tube. This boat need only be used with solids and with liquids whose boiling points lie above 200°. Other liquids are weighed in a bulb with a capillary stem about 5 cm. long. At the time of the analysis the tip of the stem is cut off, the bulb at once inserted in the tube and the cork forced home. The nitric acid boat (B) is placed 8 cm. beyond the sample boat. A free space of some 10 cm. is left beyond the nitric acid boat. Forty to 45 cm. of the tube contains fragments of pyrex glass about 1 cm.

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[1] Paper No. 171, Journal Series, University of Arkansas.

[2] Leonard, THIS JOURNAL, 45,255 **(1923).**

[3] The acid may be used for several analyses; it is quite satisfactory as long as it will freely liberate red fumes.

in diameter (made from old combustion tubes). A considerable free space is left above the chips for the passage of the gases. The receiver contains 100 cc. of water. The combustion tube is wrapped with a single layer of wire gauze over the portion containing the glass chips. This portion should be supported at intervals of 8 to 10 cm.[4] When the apparatus is set up in duplicate, both tubes are wrapped within one sheet of screening. A battery of eight Fisher burners is used to heat the tube. It has not been necessary to use oxygen with this apparatus; only air has been used and flashing (very mild) has only taken place in one or two instances with no interruption of the analysis.

At the beginning of an analysis several burners at the distal end of the tube are lighted and the sample placed in the tube. The rest of the burners are then lighted and the tube allowed to fill with brown fumes. With a very volatile sample it may be well to hasten the production of fumes by gently warming the nitric acid boat. The stream of air carrying nitrogen oxides is then passed through the apparatus; about two bubbles per second should pass the receiver. We have found it advantageous to cover the cork between the bulb (E) and the tube with "Vulcan Paste" to avoid any possibility of a leak. It is well to heat the tube near this cork at once to avoid the collection of liquid at this point, an event which may take place with an easily oxidized compound. When the pyrex chips are at red heat and the tube is completely filled with brown fumes, the sample is heated, gently at first, finally with full heat, until all liquid has been driven over and any charred matter has disappeared.

The combustion will require from one and one-half to two and one-half hours, depending upon the weight of the sample and the character of the compound. At the conclusion of a run the chips are removed from the tube and twice boiled in a beaker with small portions of water. The tube is washed a number of times with 10-cc. portions of hot water. The washings and the liquid from the receiver are combined in a 600-cc. beaker and evaporated to a volume of about 10 cc. Twenty-five cc. of concentrated hydrochloric acid is added and the liquid evaporated as before. The treatment with hydrochloric acid and evaporation is repeated, after which water is added and the solution is treated with sodium hydroxide solution until just acid to litmus. It is then

TABLE I

ANALYSIS OF SULFUR COMPOUNDS

Compound	Percentage of sulfur Calcd.	Volumetric		Gravimetric	
Butyl sulfone	17.99	17.97		17.80	
Di-*p*-tolyl sulfone	13.01	12.99	12.83	12.67	13.07
Thiourea (crude)	42.12	...	...	40.95	40.66
				41.06	41.03[a]
Butyl toluenesulfonate	14.06	13.91	13.90	14.17	14.36
Ethyl thioacetate	30.77	30.87	30.32	31.05	
Phenyl isothiocyanate	23.70	23.31	23.69	23.90	
Ethyl thiocyanate	36.78	37.17	36.71	36.71	
Methyl thiocyanate	43.83	44.31	43.82	43.76	
Tolyl isothiocyanate	21.48	21.19	21.42	21.32	
Thiophenol	29.08	28.98		28.46	28.50
Ethyl sulfide	35.55			34.93	35.13

[a] Result by another method. Analyses performed by Mr. J. G. Womack and Mr. R. H. Philbeck. Preliminary analyses by Mr. A. V. Tuller.

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[4] Our tubes were of pyrex glass. When properly supported and wrapped they could be used eight or nine times before it was necessary to reject them. A quartz tube would have a longer life.

filtered, the volume brought to 300 cc., 2 cc. of 3 N hydrochloric acid added and the precipitation of barium sulfate carried out in the usual manner.

Much time may be saved if the estimation of sulfate is performed volumetrically. In this case the filtered acid solution is brought to a volume of 200 cc. and handled as directed in a previous paper on this subject.[5]

Results

Table I cites results secured in the analysis of several organic compounds by this method. The first three compounds are solids. They were analyzed to insure that the method would handle compounds known to be difficult of oxidation or because they had been analyzed by other methods and their sulfur content was known.

Summary

The Klason method of oxidation of volatile organic liquids and solids as reported in modified form by Leonard has been altered so as to replace the expensive platinum catalyst with chips of pyrex glass. Air is used in place of oxygen, thus greatly decreasing the possibility of flashing. The method is recommended for the determination of sulfur in organic liquids and in solids for which the Parr method is unsuitable.

FAYETTEVILLE, ARKANSAS

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE. II. THE DERIVATIVES OF DERRITOL[1]

BY F. B. LAFORGE AND L. E. SMITH

RECEIVED SEPTEMBER 21, 1929 PUBLISHED MARCH 6, 1930

Catalytic hydrogenation of rotenone results in the formation of two compounds: dihydrorotenone, a neutral substance in which the original double bond is reduced, and an acid product which still contains the double bond. Both compounds on further reduction yield an acid containing four more hydrogen atoms than rotenone. The acid of formula $C_{23}H_{24}O_6$ will be referred to as rotenonic acid and its reduction product as dihydrorotenonic acid.[2]

This peculiar course of the reduction of rotenone leading to an acid product is characteristic not only of rotenone, but of several of its derivatives.

The action of zinc in alkaline solution on rotenone also results in the formation of two compounds: rotenol, in which the carbonyl group is reduced to an alcoholic group, and a yellow phenolic compound, derritol,

[5] Wertheim, THIS JOURNAL, 52, 1075 (1930).

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[1] Presented before the Division of Agricultural and Food Chemistry at the 78th Meeting of the American Chemical Society, Minneapolis, Minnesota, September 9 to 13, 1929.

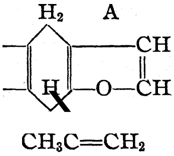
[2] LaForge and Smith, THIS JOURNAL, 51, 2574 (1929).

with composition $C_{21}H_{22}O_6$, two carbon atoms having been lost from the rotenone molecule.[3] Dihydrorotenone yields two analogous compounds.

In order to decide whether or not the same groupings were involved in these two characteristic reactions of rotenone toward two different reducing agents, derritol itself was reduced with hydrogen in the presence of platinum catalyst. In all probability it yielded dihydroderritol and derritolic acid, but since the separation of these substances was very difficult, it was found preferable first to methylate the phenolic group in order to render the neutral compound resulting from the reduction insoluble in alkali. Methyl derritol is easily obtained by the action of dimethyl sulfate on derritol in alkaline solution.

The methylated compound gave on hydrogenation a mixture of dihydromethylderritol and methylderritolic acid. From the result of this reaction it follows that the atomic groupings in rotenone which on hydrogenation react to produce an acid are not the same as those groupings which react with zinc in alkaline solution to produce derritol.

According to Takei,[4] tubaic acid, and hence rotenone, contains the atomic grouping **A.** If this formulation is correct, derritol would be expected to result by the loss of two carbon atoms from this grouping, with the formation of a phenolic radical at one of the points of attachment, although it seems strange that the double bond in the furan ring would escape reduction on catalytic hydrogenation.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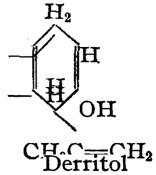
Derritol

Rotenol gives dihydrorotenol and dihydrorotenolic acid on catalytic hydrogenation.

Derritol Methyl Ether.—One gram of derritol was dissolved in the equivalent amount of 1% potassium hydroxide and 0.5 g. of dimethyl sulfate was slowly added to this solution with constant stirring. Derritol methyl ether separated out and was filtered off and recrystallized from methyl alcohol, m. p. 122°. The yield was quantitative.

Anal. Subs., 0.0609, 0.0640: CO_2, 0.1525, 0.1603. Subs., 0.0264, 0.0256; AgI, 0.0483, 0.0471. Calcd. for $C_{22}H_{24}O_6$: C, 68.75; H, 6.25; $3CH_3O$, 24.21. Found: C, 68.30, 68.32; H, 6.37, 6.32; CH_3O, 24.15, 24.31.

Reduction of Derritol Methyl Ether.—One gram of derritol methyl ether was reduced in ethyl acetate solution, 0.2 g. of platinum oxide catalyst[5] previously saturated with hydrogen being used. The theoretical volume of hydrogen corresponding to 1 molecule is 58.4 cc. The solution absorbed 60 cc. in a few minutes, after which the rate became very slow. The reaction was stopped at this point.

The solution was filtered and after the ethyl acetate had been boiled off the residue was taken up in ether and the ether solution extracted with 2% potassium hydroxide

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[3] Butenandt, *Ann.*, 464, 274 (1928).

[4] S. Takei, *Abstracts from Bull. Inst. Physical and Chemical Research (Japan)*, *8*, 64 (1929).

[5] R. Adams and R. L. Shriner, THIS JOURNAL, 45, 2171 (1923).

solution. The ether solution was washed with water, dried over anhydrous sodium sulfate and the solvent was evaporated. The compound, dihydroderritol methyl ether, was recrystallized from 95% ethyl alcohol, m. p. 107°, yield 0.17 g.

Anal. Subs., 0.0735: CO_2, 0.1838; H_2O, 0.0445. Subs., 0.0197; AgI, 0.0358. Calcd. for $C_{22}H_{26}O_6$: C, 68.39; H, 6.74; $3CH_3O$, 24.1. Found: C, 68.19; H, 6.73; CH_3O, 24.0.

The aqueous alkaline solution was acidified with hydrochloric acid, extracted with ether and the ether solution was dried over sodium sulfate. The compound methylderritolic acid was recrystallized from benzene; m. p. 154–156°; yield, 0.75 g.

Anal. Subs., 0.0775, 0.0521: CO_2, 0.1935, 0.1305; H_2O, 0.0483, 0.0329. Subs., 0.0203: AgI, 0.0379. Calcd. for $C_{22}H_{26}O_6$: C, 68.39; H, 6.74; $3CH_3O$, 24.1. Found: C, 68.07, 68.31; H, 6.92, 7.01; CH_3O, 24.66.

Oxime of Derritol Methyl Ether.—One-half gram of derritol methyl ether was refluxed for four hours with 0.4 g. of hydroxylamine hydrochloride and 0.5 g. of anhydrous sodium acetate in absolute ethyl alcohol. Upon dilution with water, the oxime crystallized out and was recrystallized from dilute ethyl alcohol, m. p. 172–173°.

Anal. Subs., 0.0565: CO_2, 0.1371; H_2O, 0.0333. Subs., 0.0203: AgI, 0.0355. Calcd. for $C_{22}H_{25}O_6N$: C, 66.16, H, 6.26; $2CH_3O$, 23.3. Found: C, 66.16; H, 6.55; CH_3O, 23.09.

Reduction of Rotenol.—One gram of rotenol was reduced with hydrogen in ethyl acetate solution; 0.2 g. of platinum oxide catalyst was used. The theoretical volume of hydrogen corresponding to 1 molecule is 56.6 cc. The solution absorbed about 75 cc. very rapidly, after which the rate of absorption began to decrease. It was found that if the reaction was stopped at this point the alkali-soluble product was a mixture of two acids. The reaction was, therefore, prolonged until 90 cc. of hydrogen had been absorbed. The ethyl acetate was evaporated off and the residue dissolved in ether and divided into neutral and acid parts. The neutral portion proved to be dihydrorotenol identical with that prepared from dihydrorotenone.[2] The yield was 0.15 g. The acid portion, dihydrorotenolic acid, was recrystallized from dilute ethyl alcohol. It melted between 76 and 80°, and probably contained an indefinite amount of solvent. The yield was 0.75 g. For analysis it was dried to constant weight at about 90°.

Anal. Subs., 0.0560, 0.0494: CO_2, 0.1415, 0.1249; H_2O, 0.0352, 0.0305. Subs., 0.0223: AgI, 0.0264. Calcd. for $C_{23}H_{28}O_6$: C, 69.0; H, 7.0; $2CH_3O$, 15.5. Found: C, 68.92, 68.95; H, 6.74, 6.86; CH_3O, 15.64.

Summary

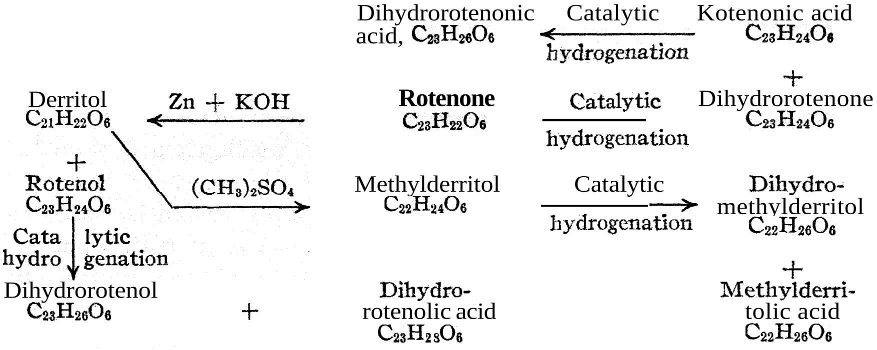
Both derritol and rotenol give mixtures of neutral and acid products on catalytic hydrogenation.

In the case of derritol, which is itself a phenolic compound, it was necessary to methylate the phenol group for convenience in separating the acid. Dihydromethylderritol and methylderritolic acids were the products of the reduction.

Rotenol gave dihydrorotenol and rotenolic acid. The latter was further reduced to dihydrorotenolic acid,

These results indicate that the atomic groupings which react to form derritol from rotenone are not the same as those which are involved in the formation of acids from rotenone and many of its derivatives.

The reactions involved are illustrated in the diagram shown below.



WASHINGTON, D. C.

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE. III. DEHYDROROTENONE[1]

BY F. B. LAFORGE AND L. E. SMITH

RECEIVED SEPTEMBER 21, 1929 PUBLISHED MARCH 6, 1930

Butenandt[2] has shown that a number of oxidizing agents, such as permanganate, potassium ferricyanide, perbenzoic acid and iodine with potassium acetate in alcoholic solution, convert rotenone into dehydrorotenone with a loss of two hydrogen atoms.

Dehydrorotenone is a yellow crystalline compound melting at about 225° and differing widely from rotenone in most of its reactions. Compounds corresponding to dehydrorotenone are easily obtainable from dihydrorotenone and isorotenone. Dehydrorotenone contains the original double bond and carbonyl group of rotenone, but unlike rotenone, it is not decomposed by alkalies, nor does it yield a compound corresponding to derritol. On treatment with alkali or with zinc in alkaline solution, it takes up two molecules of water and is converted into an acid[2] $C_{23}H_{24}O_8$ which for future reference we would like to call dehydrodihydroxyrotenonic acid.

When rotenone is subjected to treatment with stronger oxidizing agents, such as chromic or nitrous acid, the resulting product is a bright yellow compound, rotenonone, having the composition either $C_{23}H_{20}O_7$ or $C_{23}H_{18}O_7$. It is sometimes difficult to prepare rotenonone in a pure state since hydrochloric acid is likely to be added to the double bond. However, dihydrorotenone readily yields dihydrorotenonone on treatment with nitrous acid and corresponding compounds are easily obtained from isorotenone, rotenonic and dihydrorotenonic acids.

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[1] Presented before the Division of Agricultural and Food Chemistry at the 78th Meeting of the American Chemical Society, Minneapolis, Minn., September 9 to 13, 1929.

[2] Butenandt, *Ann.*, **464**, 270 (1928).

Butenandt assumed that rotenonone was an α,α-diketone, because it gave an hydroxy acid on treatment with alkali. He interpreted this reaction as a benzilic acid rearrangement. Takei,[3] who first prepared rotenonone, assumed that the formation of the hydroxy acid was due to the opening of a lactone ring. This last-mentioned assumption is probably correct, because neither rotenonone nor any of the corresponding compounds are affected by strong hydrogen peroxide, as would be expected if they were α,α-diketones; moreover, they do not react with *o*-phenylenediamine. All of these diketones are derivatives of dehydrorotenone and not of rotenone itself, for the same diketone is formed from dehydrorotenone as from rotenone, and dihydrodehydrorotenone yields the same diketone as does dihydrorotenone, showing that the formation of the dehydro compounds has preceded the formation of the diketones and that they are derivatives of the dehydro series.

Although dehydrorotenone does not yield compounds corresponding to derritol, it behaves similarly to rotenone on catalytic reduction and yields an acid as the main product.

The most satisfactory method for the preparation of dehydrorotenone is by the addition of iodine to a hot alcoholic solution of rotenone and potassium acetate. Dehydrorotenone crystallizes out on cooling. The same method is used to prepare all other dehydro derivatives.

The yields of the dehydro compounds are generally about 35% of the theoretical. Butenandt made only a very small quantity of dehydrorotenone by the iodine method and failed to notice that it was not the main product of the reaction. The mother liquors from the dehydrorotenone crystallization yield a crystalline residue on evaporation, which after washing with water and recrystallization amounts to more than half of the weight of rotenone employed.

The compound is the acetate of an alcohol of formula $C_{23}H_{22}O_7$. The alcohol itself, which will be called rotenolone, is easily isolated by saponification of the acetate.

Either the acetate or the alcohol is readily converted into dehydrorotenone by boiling with about 5% alcoholic sulfuric acid. It seems very likely that the first step in the reaction is the substitution of a hydrogen atom by iodine, the resulting compound then reacting with potassium acetate. Since the acetate or the alcohol which is isolated is converted into dehydrorotenone only with some difficulty, it seems likely that two isomeric hydroxy compounds are produced with the formation of a new asymmetric carbon atom and that the hydroxyl of one is more favorably situated for reaction with another hydrogen atom to form the dehydro compounds.

Takei in his most recent publication[4] has proposed a formula for tubaic

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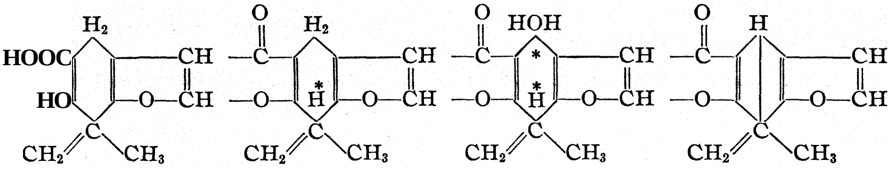
[3] Takei, *Biochem. Z.*, 157, 14 (1925).

[4] Takei, *Bull. Inst. Phys. Chem. Res.*, 8, 519 (1929).

acid which incidentally offers an explanation for the formation and properties of the dehydro compounds



Tubaic acid Rotenone Rotenolone Dehydrorotenone

Rotenolone yields ordinary rotenol and derritol on treatment with zinc in alkaline solution.

As previously stated, dehydrorotenone yields an acid of formula $C_{23}H_{24}O_8$. This acid is probably formed by the hydrolysis of both the lactone and ether linkages which are very likely present in the molecule.

The probable connection between the grouping contained in tubaic acid and the rest of the molecule is represented by a chain containing the carbonyl group.

Cleavage of this chain can be effected by oxidation with hydrogen peroxide in alkaline solution. By this treatment a dibasic acid is obtained which corresponds to the portion of the rotenone molecule containing the original methoxyl groups of rotenone and is represented by the formula $C_{12}H_{14}O_7$. It will be named "derric acid." As this formula contains one more oxygen atom than would be expected, it is probable that one is in the form of an hydroxyl group which is not present in the acid from which it is prepared.

Dehydrorotenone.[2]—Twelve grams of rotenone and 30 g. of potassium acetate are dissolved in about 300 cc. of hot absolute alcohol and about 10 g. of iodine in hot alcoholic solution is added in small portions. The iodine is absorbed rapidly until toward the end of the reaction when dehydrorotenone begins to crystallize at once from the hot solution. After cooling and filtering, the alcoholic solution is evaporated to a very small volume in an open dish on the steam-bath. The residue crystallizes in a short time and is washed with water to remove the salts.

Acetylrotenolone.—The crystalline mass insoluble in water may be dissolved in ether, generally leaving a small quantity of dehydrorotenone. The solution is dried and evaporated, or it may be directly recrystallized from absolute alcohol, or benzene and petroleum ether, from which it crystallizes in thin prisms. The yield amounts to about 6 g. of pure material, melting sharply at 184".

And. Subs., 0.0693: CO_2, 0.1684; H_2O, 0.0338. Subs., 0.0213, 0.0214: AgI, 0.0230, 0.0214. Subs., 0.7182: 3.1 cc. of *N*/2 alkali. Calcd. for $C_{25}H_{24}O_8$: C, 66.37; H, 5.31; $2CH_3O$, 13.73; acetyl, 9.5. Found: C, 66.12; H, 5.42; CH_3O, 14.25; acetyl, 9.3.

The substance is the acetyl derivative of a compound which contains one oxygen more than rotenone and which will be named rotenolone.

Rotenolone.—Three grams of acetyl rotenolone was boiled for two hours with about 25 cc. of *N*/2 alcoholic potassium hydroxide solution. Addition of dilute hydrochloric acid or water gave a white semi-crystalline product, which was dissolved in ether. After drying, the ether was evaporated, leaving a glassy mass which, however, began to crystallize in a few days. On being stirred with methyl alcohol, it all became crystalline. The compound was washed with a very little methyl alcohol and recrystallized from about 8 parts of the same solvent. The yield was 2.25 g. of recrystallized material—82% of the theoretical. The compound consists of short, very heavy prisms of unusually perfect form, m. p. 140–141°.

Anal. Subs., 0.0681: CO_2, 0.1677; H_2O, 0.0334. Subs., 0.0202: AgI, 0.0229. Calcd. for $C_{23}H_{22}O_7$: C, 67.31; H, 5.36; $2CH_3O$, 15.1. Found: C, 67.15; H, 5.44; CH_3O, 14.9.

Both rotenolone and its acetate are converted quantitatively into dehydrorotenone by boiling with about 5% alcoholic sulfuric acid.

For the preparation of dehydrorotenone the crude acetate may be employed, and a total yield of about 75% of the rotenone taken may be obtained.

Dehydrodihydrorotenone.—One gram of dihydrorotenone together with 2.5 g. of potassium acetate was dissolved in 25 to 30 cc. of alcohol, and 0.7 g. of iodine in alcoholic solution was added to the hot solution in small portions. Dehydrodihydrorotenone separated out even from the hot solution. The yield was 0.35 g. It was recrystallized from absolute alcohol and dried at 110'. It forms thin pale yellow prisms which melt at 228–230°.

Anal. Subs., 0.0701, 0.0700: CO_2, 0.1790, 0.1785; H_2O, 0.0362, 0.0364. Subs., 0.0193: AgI, 0.0219. Calcd. for $C_{23}H_{22}O_6$: C, 70.05; H, 5.60; $2CH_3O$, 15.80. Found: C, 69.83, 69.70; H, 5.74, 5.78; CH_3O, 15.75.

The alcoholic mother liquor gave a flocculent precipitate when diluted with water. It was taken up in ether, separated from water and washed to remove alcohol. On evaporation the dried ethereal solution yielded a colorless sirup which crystallized on being rubbed with methyl alcohol. It was recrystallized once from methyl alcohol and then from benzene and petroleum ether. It is the acetate of dihydrorotenolone and forms colorless plates, melting at 189°.

Anal. Subs., 0.0700: CO_2, 0.1693; H_2O, 0.0365. Subs., 0.0206, 0.0216: AgI, 0.0219. 0.0226. Calcd. for $C_{25}H_{26}O_8$: C, 66.10; H, 5.73; $2CH_3O$, 13.66. Found: C, 65.90; H, 5.79; CH_3O, 13.95, 13.85.

The substance gives dehydrodihydrorotenone on boiling with alcoholic sulfuric acid.

Dehydroisorotenone.—One-half gram of isorotenone was treated with iodine and potassium acetate in exactly the same manner as dihydrorotenone and yielded 0.1 g. of yellow prisms. Recrystallized from alcohol it melted at 195°. On evaporation of the alcoholic solution a semi-crystalline mass was obtained which gave dehydroisorotenone on boiling with alcoholic sulfuric acid.

Anal. Subs., 0.0710: CO_2, 0.1840; H_2O, 0.0347. Calcd. for $C_{23}H_{20}O_6$: C, 70.37; H, 5.15. Found: C, 70.68; H, 5.43.

Dehydrodihydrorotenonic Acid.—Two grams of dehydrorotenone dissolved in 40 cc. of ethyl acetate was reduced with hydrogen and platinum catalyst in the usual manner. Two hundred and twenty-five cc. of hydrogen, which is about the theoretical volume corresponding to 2 molecules, was absorbed in one and one-half hours. The filtered solution yielded a crystalline product on evaporation which was agitated with 2% potassium hydroxide solution and filtered from a small residue. The aqueous solutions yielded a voluminous crystalline precipitate on acidification which was filtered off and recrystallized by dissolving in 25 cc. of hot alcohol and adding an equal volume of hot water. The compound consists of yellow needles, melting at 223'. The yield was 1.8 g.

Anal. Subs., 0.0790, 0.0687: CO_2, 0.2013, 0.1749; H_2O, 0.0414, 0.0372. Calcd. for $C_{23}H_{24}O_6$: C, 69.68; H, 6.06. Found: C, 69.46, 69.57; H, 6.82, 6.01.

The product insoluble in alkali formed flat pointed prisms from alcohol, but the quantity was too small for further study.

Dihydrorotenonone (Dehydrodihydrorotenonone).—Three grams of dihydrorotenone was dissolved in glacial acetic acid and to the solution, which was cooled with ice, 9 g. of amyl nitrite was added. To this mixture 6 cc. of concentrated hydrochloric acid in 6 cc. of acetic acid was slowly added. On warming to room temperature, the dihydrorotenone crystallized out. It was recrystallized from acetic acid, m. p., 272–275°, with decomposition; yield, 1.95 g.

Anal. Subs., 0.0589: CO_2, 0.1457; H_2O, 0.0277. Subs., 0.0211: AgI, 0.0232. Calcd. for $C_{23}H_{22}O_7$: C, 67.31; H, 5.36; $2CH_3O$, 15.12; for $C_{23}H_{20}O_7$: C, 67.61; H, 4.93; $2CH_3O$, 15.19. Found: C, 67.44; H, 5.22; CH_3O, 14.52.

Dihydrodehydrohydroxyrotenononic Acid.—One gram of dihydrorotenonone was placed in a flask with 1 g. of solid potassium hydroxide. Enough water to dissolve the potassium hydroxide was put in and an equal volume of alcohol was then added. The mixture was boiled for a few minutes until the dihydrorotenonone had dissolved. The acid was precipitated from the solution with hydrochloric acid. The yield was 0.57 g. Recrystallized from dilute acetic acid, it melted at 257°.

Anal. Subs., 0.0568: CO_2, 0.1346; H_2O, 0.0280. Subs., 0.0210: AgI, 0.0228. Calcd. for $C_{23}H_{24}O_8$: C, 64.48; H, 5.60; $2CH_3O$, 14.48; for $C_{23}H_{22}O_8$: C, 64.79; H, 5.17; $2CH_3O$, 14.54. Found: C, 64.61; H, 5.48; CH_3O, 14.34.

Dehydrodihydrorotenonone.—The same procedure was employed for this preparation as the one described above. The proportions employed were: 0.6 g. of dehydrodihydrorotenone, 1.2 cc. of hydrochloric acid and 1.8 g. of amyl nitrite. The compound was recrystallized from a large volume of alcohol. The yield was 0.5 g. melting at 273°.

Anal. Subs., 0.0715: CO_2, 0.1774; H_2O, 0.0325. Subs., 0.0200: AgI, 0.0233. Calcd. for $C_{23}H_{20}O_7$: C, 67.61; H, 4.93; $2CH_3O$, 15.20. Found: C, 67.65; H, 5.06; CH_3O, 15.38.

Dehydrodihydrorotenonone is identical with the corresponding compound obtained from dihydrorotenone. Both have the same melting point and a mixed melting point determination showed no depression. Their identity was established beyond doubt by a crystallographic examination by George L. Keenan, of the Food, Drug and Insecticide Administration of the Department of Agriculture.

"Dihydrorotenonone and dehydrodihydrorotenonone were found to have identical optical properties. Both samples consist of fine needles with a yellowish tinge when examined in ordinary light under the microscope. In parallel polarized light (crossed Nicols) the extinction is straight and the sign of elongation +. The refractive indices are: n = 1.476 (always lengthwise); n = indetd.; n = 1.733. An intermediate index value, n_i = 1.733 occurs frequently on needles crosswise. All indices ±0.003."

Isorotenonone (Dehydroisorotenonone).—The reaction with isorotenone was carried out identically as in the preparation of dihydrorotenonone. With 2.0 g. of isorotenone, 1.2 g. of isorotenonone was obtained in the form of yellow silky needles.

Anal. Subs., 0.0578: CO_2, 0.1434; H_2O, 0.0233. Subs., 0.0218: AgI, 0.0246. Calcd. for $C_{23}H_{20}O_7$: C, 67.61; H, 4.93; $2CH_3O$, 15.19; for $C_{23}H_{18}O_7$: C, 67.98; H, 4.43; $2CH_3O$, 15.27. Found: C, 67.62; H, 4.48; CH_3O, 14.91.

Rotenol and Derritol from Acetylrotenolone.—Three grams of acetylrotenolone was dissolved in 90 cc. of alcohol and 30 cc. of 15% potassium hydroxide was added. After boiling for about one minute, 6 g. of zinc dust was added, and the solution was boiled under reflux for about four hours. Dilute hydrochloric acid was added to the cooled solution and the precipitate dissolved in ether. The ethereal solution was extracted with dilute alkali and the aqueous solution acidified. The precipitated material was dissolved in ether, the solvent dried and evaporated. The sirupy residue crystallized when rubbed with methyl alcohol and the crystalline material was recrystallized from 50% alcohol. The yield was 0.9 g. It proved to be ordinary derritol, melting at 163° and showing no depression when melted with derritol from rotenone.

Anal. Subs., 0.0707: CO_2, 0.1771; H_2O, 0.0380. Calcd. for $C_{21}H_{22}O_6$: C, 68.07; H, 5.99. Found: C, 68.31; H, 5.97.

The ethereal solution containing the alkali-insoluble fraction yielded 1 g. of rotenol which on recrystallization melted at 121°, and showed no depression when mixed with rotenol from rotenone.

Anal. Subs., 0.0675: CO_2, 0.1724; H_2O, 0.038. Calcd. for $C_{23}H_{24}O_6$: C, 69.67; H, 6.06. Found: C, 69.66; H, 6.26.

Dehydrodihydroxyrotenonic Acid.—It was found that the procedure given by Butenandt for the preparation of dehydrodihydroxyrotenonic acid gave very poor yields, and owing to excessive tar the product was difficult to purify. The procedure used in the preparation of rotenol and derritol[5] gave much better results. Four grams of dehydrorotenone was refluxed with 40 cc. of 15% potassium hydroxide, 120 cc. of ethyl alcohol and 8 g. of zinc dust for two hours. The zinc was removed by filtration and the solution acidified with dilute hydrochloric acid. Water was added to the hot solution until crystallization started and then the solution was cooled in an ice-bath. This gave a fairly pure product which was recrystallized from dilute ethyl alcohol; yield, 2.5 g.; m. p. 157°.

Dehydrodihydrorotenononic Acid.—Six grams of dihydrorotenonic acid was dissolved in 50 cc. of glacial acetic acid, the solution cooled in an ice-bath and 18 g. of amyl nitrite added. A mixture of 12 cc. of concentrated hydrochloric acid and 12 cc. of acetic acid was added slowly over a period of about forty-five minutes. The flask was then allowed to come to room temperature. Crystallization began after about one hour and proceeded rapidly with gas and heat evolution and the flask soon became filled with a yellow crystalline mass. As soon as the gas evolution had ceased the product was filtered off. The yield is diminished if the product is allowed to stand for very long.

The compound is very difficultly soluble in all reagents but may be recrystallized from acetic acid. The yield was 5 g. The melting point is very high and it was not accurately determined.

Anal. Subs., 0.0575: CO_2, 0.1414; H_2O, 0.0288. Subs., 0.0189: AgI, 0.0216. Calcd. for $C_{23}H_{22}O_7$: C, 67.32; H, 5.37; $2CH_3O$, 15.06. Found: C, 67.23; H, 5.57; CH_3O, 15.08.

Oxidation of **Dehydrodihydroxyrotenonic** Acid to Derric Acid.—One gram of acid was dissolved in 10 cc. of 5% potassium hydroxide. This solution was heated nearly to boiling in a 400-cc. beaker and 3 g. of 30% hydrogen peroxide was added slowly. The solution turned very dark and effervesced considerably. With the addition of the last of the hydrogen peroxide, the solution became somewhat lighter in color, although with some runs there was a slight amount of charring. The reaction is complete when acid produces no precipitate from a diluted test portion. The solution is acidified with hydrochloric acid, producing a precipitate in the concentrated solution. A high concentration facilitates extraction of the reaction products with ether. The ether extract from this solution is dried over sodium sulfate and on evaporation gives an oil which slowly crystallizes. As the crystallization is never complete, the crystals are separated from the oily by-products by pressing between filter papers. The small amount of remaining oil can be removed with chloroform. The compound is then

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[5] LaForge and Smith, THIS JOURNAL, 51, 2579 (1929).

recrystallized from n-butyl ether. The yields averaged **0.15** g.; m. p. **169"**. The compound is soluble in water, giving an acid reaction to litmus. It is also soluble in methyl, ethyl and butyl alcohols, ethyl acetate and acetic acid, but insoluble in chloroform, carbon tetrachloride, benzene, toluene and carbon disulfide. It gives no phenol test with ferric chloride.

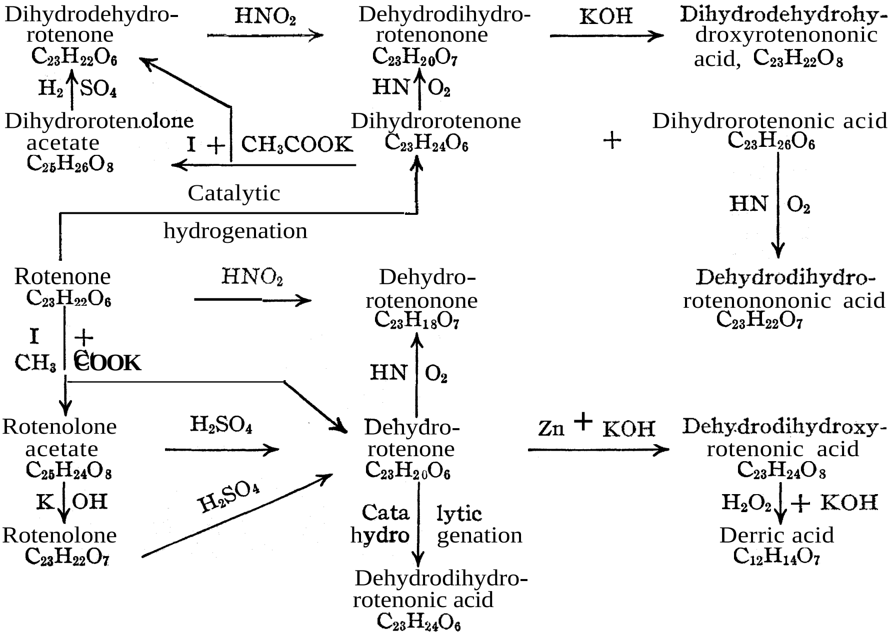
Anal. Subs., **0.0521, 0.0510:** CO_2, **0.1008, 0.0996;** H_2O, **0.0246, 0.0245.** Subs., **0.0203, 0.0201:** AgI, 0.0349, **0.0349.** Calcd. for $C_{12}H_{14}O_7$: C, **53.33;** H, **5.18;** $2CH_3O$, **22.96.** Found: C, **52.77, 53.26;** H, **5.24, 5.33;** CH_3O, **22.71, 22.93.** Titration: **0.0202** g. used **1.5** cc. of **0.1002** *N* **KOH; mol.** wt. calcd., **270;** found for dibasic acid, **269.**

Summary

Dehydrorotenone and the corresponding compounds of the dehydro series are best prepared by the action of iodine and potassium acetate on rotenone and other of its derivatives. A portion of the dehydrorotenone derivatives is obtained directly, but the main product of the reaction is an acetyl derivative of a compound $C_{23}H_{22}O_7$ (in the case of rotenone itself), which yields an hydroxyl derivative on saponification. This compound loses water on boiling with alcoholic sulfuric acid and is converted into dehydrorotenone.

Rotenonone and other diketones prepared by oxidation from rotenone, etc., are derivatives of the dehydro series.

Rotenolone, the hydroxy derivative of rotenone, yields derritol and rotenol on treatment with zinc in alkaline solution.



REACTIONS INVOLVED

Dehydrodihydroxyrotenonic acid of formula $C_{23}H_{24}O_8$, prepared from dehydrorotenone by the action of zinc and alkali or alkali alone, according to the directions of Butenandt, was oxidized with hydrogen peroxide in alkaline solution, and yielded a dibasic acid of formula $C_{12}H_{14}O_7$, which represents that half of the rotenone molecule which carries the original methoxyl groups as well as the carboxyl that in rotenone is coupled with the other half of the molecule to form the lactone group. The second carboxyl is formed by oxidation of the original carbonyl group.

The dibasic acid has been called "derric acid."

WASHINGTON, D. C.

[CONTRIBUTION FROM THE RESEARCH AND BIOLOGICAL LABORATORIES OF E. R. SQUIBB AND SONS]

THE RATE OF THERMAL DECOMPOSITION OF THE OXYTOCIC PRINCIPLE OF THE POSTERIOR LOBE OF THE PITUITARY GLAND. II. THE EFFECT OF TEMPERATURE

BY TILLMAN D. GERLOUGH AND ROBERT W. BATES

RECEIVED SEPTEMBER 24, 1929 PUBLISHED MARCH 6, 1930

This paper deals with the effect of temperature on the rate of thermal decomposition of the oxytocic principle in pituitary extract and of the highly purified oxytocic principle. Such a study has important bearing on problems concerned with its manufacture, and is of additional interest in determining whether or not further purification alters the rate of destruction of the oxytocic principle.

Experimental Methods

The oxytocic solutions and methods employed were much the same as those described in Paper I.[1] Pituitary solution No. 10122 was prepared by extracting the acetone defatted posterior lobe with acetic acid. This unpurified solution contains, in addition to the oxytocic principle, the pressor principle in nearly the same unitage as the oxytocic, inert proteins and a trace of salts. The purified oxytocic principle was prepared by the method of Kamm and co-workers[2] Its composition is largely oxytocic protein with a small quantity of pressor principle and a very small trace of ammonium salt. Nitrogen determinations showed that the purified solution contained 0.0075 mg. of protein nitrogen per 10 international units, while the pituitary solution No. 10122 contained 0.29 mg. of nitrogen per 10 units.

The solution of the purified oxytocic principle, which had been previously assayed, was divided into two parts, (A) and (B). (A) was made by diluting with 0.2% acetic acid and (B) was made by diluting with

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[1] Gerlough, THIS JOURNAL, 52, 824 (1930).

[2] Kamm, Aldrich, Grote, Rowe and Bugbee, *ibid.*, 50, 573 (1928).

0.1% acetic acid. The reaction of (A) was set at PH 3.35 and that of (B) was *P*H 3.55. Before starting the destruction work all solutions were placed in hard glass ampules, sealed and sterilized in streaming steam. The oxytocic activity of each solution, (A), (B) and No. 10122, was now 10 international units per cc. or 100% U. S. P. X. Some of the sterilized ampules were withheld as controls and kept at 2°. The remaining ampules were then heated at the temperatures shown in Table I and also held at 2° prior to actual test. Since the rate of destruction is so extremely slow at this temperature, no appreciable change would occur which might influence the results during the period of testing. The PH of all heated solutions did not increase more than 0.05 from their controls. The temperatures recorded are accurate within 0.5°.

TABLE I

RATE OF THERMAL DECOMPOSITION OF THE OXYTOCIC PRINCIPLE AT VARIOUS TEMPERATURES

Pituitary Solution, No. 10122, **PH** 3.25

T, °.	t, hours	$a - x$	K	Log $1/k$	u
...	0.0	1.00	......	..	....
308.8	1699.0	0.83	0.000109	3.96	20,500
325.6	696.0	.70	.000512	3.29	21,300
337.8	262.0	.70	.00140	2.85	22,500
351.6	95.0	.63	.00486	2.31	23,400
361.1	43.0	.66	.00965	2.01	25,500
373.1	....	..	.0333[a]	1.48	....
...	....	..	......	..	24,000
394.1	0.75	.87	.185	0.732	
					Av. 22,900
	(A) Purified Oxytocic Principle, *P*H 3.35				
...	0.0	1.00	......	..	....
309.1	2568.0	0.84	0.0000677	4.16	22,200
342.1	120.0	.77	.00217	2.66	22,300
358.6	48.5	.65	.00887	2.05	24,000
373.1	8.0	.77	.0326	1.49	
					Av. 22,800
	(B) Purified Oxytocic Principle, PH 3.55				
...	0.0	1.00	......	..	....
309.1	2568.0	0.73	0.000122	3.91	22,100
342.1	120.0	.69	.00309	2.51	23,800
358.6	48.5	.52	.0134	1.87	25,600
373.1	8.0	.64	.0557	1.25	
					Av. 23,800

[a] The value recorded in Paper I averaged with those found by later experiments.

Assay of the oxytocic activity remaining in the solution after destruction was made according to the method of Dale and Laidlaw,[3] employing

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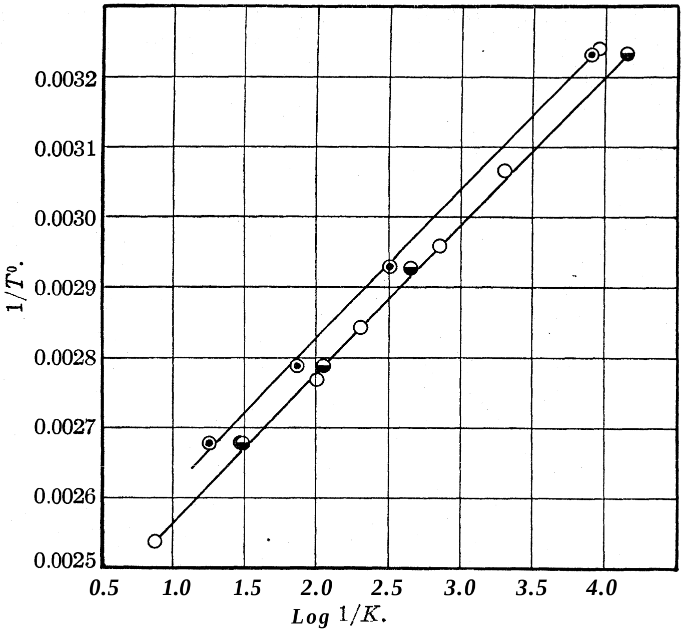
[3] Dale and Laidlaw, *J. Pharmacol Exptl. Therap.*, 4, 75 (1912).

the Locke solution recommended by the U. S. P. X. One of us (R. W. B.) assayed and interpreted the results on the decomposition of Pituitary Solution No. 10122 while the other (T. D. G.) purified and assayed Solutions (A) and (B) a number of months later and made his interpretations independently.

The average number of uterus muscles used in arriving at the value of the amount destroyed at each temperature for each type of pituitary solution was as follows: Solution No. 10122, three; Solution (A), five; Solution (B), four.



○, Pituitary soln. *10122*, PH *3.25;* ⊖, purified oxytocic principle, *PH, 3.35;* ◉, purified oxytocic principle, PH, *3.55.*

Fig. 1.—Effect of temperature on the rate of destruction of oxytocic principle.

Experimental Results

All of the experimental results are given in Table I and expressed graphically in Pig. 1. In Col. 3, $a - x$ represents the amount of oxytocic activity remaining after thermal destruction had occurred. Time, t, is expressed in hours and the rate of destruction, K, calculated from the equation, $K = 1/t\ 2.3 \log a/(a - x)$. The justification for this method of calculating the rate constants has been given in a previous paper. For convenience in plotting, log $1/k$ is used instead of k, and is recorded in Col. 5. The influence of temperature on the rate of change of the reaction velocity as represented by the constant u (see Col. 6) has been computed from the

Arrhenius empirical equation, [illegible] $= 2\left(\frac{T_0T_1}{T_1 - T_0}\right) 2.3 \log \frac{k_1}{k_0}$, which has been shown to hold for many types of irreversible reactions within a comparatively short range of temperature. These values were calculated for all temperature differences between 35.7 and 100°, and between 100 and 121°.

Discussion

Purification did not noticeably alter the stability of the oxytocic principle in the temperature ranges employed, although Solution (A) had 1/30 to 1/40 of the nitrogen content of Solution No. 10122. Both solutions had, as nearly as we could determine, the same rate of destruction. The difference in the P_H of these two solutions is of no real consequence, since they are both within the range of maximum stability, P_H 3.0 to 3.4. Too much emphasis should not be placed on any particular value, due to difficulties involved in the assay. Nevertheless, we believe that the data, taken as a whole, represent fairly accurately the thermal decomposition of the oxytocic principle (see Fig. 1).

Since the rate of change with temperature is reasonably constant between 36 and 121°, we feel justified in assuming that our results can be extrapolated to lower temperatures, that is, 0 to 20°, giving values indicating an exceedingly slow rate of destruction, which would harmonize with the general opinion of Smith and McClosky[5] that very little or no destruction could be detected in solutions held at temperatures below 37° over a period of six months.

The rate of destruction of Solution (B) was studied at P_H 3.55, which is slightly alkaline to the point of maximum stability of pituitary extract. It would, therefore, together with Solution (A) serve as a check as to whether or not the relationship between P_H and rate of destruction held for purified solution in the same degree as that found for the pituitary extract shown in Paper I. The rate of destruction of oxytocic principle in Solution (B) should be faster than that for (A). Such was found to be the case and the check at 100° was reasonably close to the value interpolated from Fig. 2 in Paper I at P_H 3.55. The value of log $1/k$ is 1.26 (interpolated) for the extract and 1.25 (observed) for the purified 100° solution.

Summary

1. The rate of thermal destruction of the oxytocic principle at various temperatures between 35.7 and 121° was determined.

2. Purification of pituitary extract did not alter the thermal stability of the oxytocic principle.

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[4] Arrhenius, "Quantitative Laws in Biological Chemistry," Bell and Sons, London, 1915.

[5] Smith and McClosky, *U S P. H* Bull, Hyg. Lab., No 138 (1924).

3. At PH 3.25 to 3.35 the temperature coefficient $u = 23{,}000$, while at *PH 3.55*, $u = 24{,}000$.

NEW BRUNSWICK, NEW JERSEY

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE. IV. CONSTITUTION OF ROTENONE

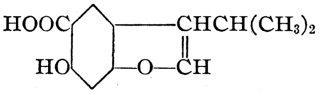
BY F. B. LAFORGE

RECEIVED SEPTEMBER 25, 1929 PUBLISHED MARCH 6, 1930

Up to the present it has not seemed advisable to propose a constitutional formula for rotenone. This has not been because data were lacking, for a very large number of rotenone derivatives have been prepared and several unusual reactions peculiar to rotenone have been observed, but until the recent publication of Takei's[1] formula for tubaic and rotenic acids, the particular key fact had been missing. About a year ago Butenandt[2] published an article in which he stated that a constitutional formula for rotenone must fulfil the following requirements.

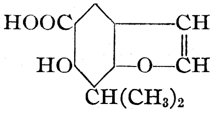
"It must explain: (1) the optical activity; (2) the indifference toward methylmagnesium iodide, ferric chloride, diazomethane and acetic anhydride; (3) the reduction of Fehling's solution; (4) the formation of two groups of structurally different oximes and hydrazones; *(5)* the formation of dehydrorotenone by loss of two hydrogen atoms and the conversion of this compound to a monocarboxylic acid by addition of two moles of water; (6) the cleavage of rotenone to derritol, a yellow phenol containing two atoms of carbon less than rotenone; (7) the cleavage of rotenone to tubaic acid; (8) the formation of a monocarboxylic acid $C_{23}H_{26}O_6$ by hydrogenation in ammoniacal solution."

At the time of Butenandt's publication the structure of tubaic acid had not been determined, although Takei[3] had tentatively proposed the formula

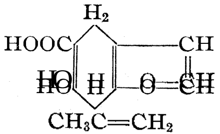


for rotenic acid. Derric acid,[4] which corresponds to the half of the rotenone molecule that carries the methoxyl groups, had not yet been isolated.

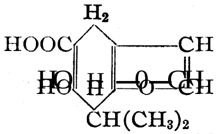
In his most recent article, Takei[1] has proposed the following formulas



Rotenic acid



Tubaic acid



Dihydrotubaic acid

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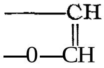
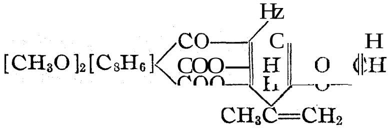
[1] Takei, *Bull. Inst. Phys. Chem. Res.*, 8, 519 (1929).

[2] Butenandt, Ann., 464, 270 (1928).

[3] Takei, Ber., 61, 2943 (1928).

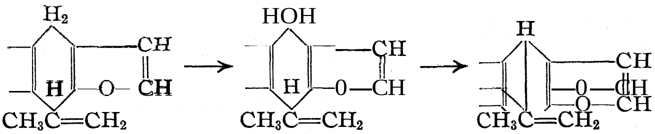
[4] LaForge and Smith, THIS JOURNAL, 52, 1091 (1930).

He gives very good reasons in support of these formulas, at least in so far as the nature of the nucleus contained in tubaic acid is concerned. The peculiar nature of the nucleus postulated is sufficient to explain the known reactions of tubaic, dihydrotubaic and rotenic acids. Not only does it explain the reactions of these acids but, taking into consideration the formation and the nature of derric acid, a formula for the entire rotenone molecule may be proposed which fulfils all of the conditions imposed by Butenandt, without a single known discordant fact, as well as explains certain new facts which we ourselves have observed. In this formula several details concerning the structure of the part of the molecule which gives derric acid still remain to be worked out and, as far as we know, the positions of attachment of the grouping  $\begin{matrix} \text{——CH} \\ \| \\ \text{—O—CH} \end{matrix}$ in tubaic acid are still uncertain,



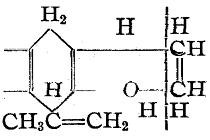
Rotenone

A compound of this formula would have the following characteristics: (1) it would be optically active; (2) it would contain no hydroxyl group to react with methylmagnesium iodide, ferric chloride, acetic anhydride, etc.; (3) it would have a ketone group and would be expected to reduce Fehling's solution; (4) the formation of the structurally different oximes and hydrazones would be expected to take place by the opening of the lactone ring with formation of a phenol group and a carboxyl group, the latter reacting to form a new ring system, as suggested by Butenandt himself;[2] (5) we have already discussed the formation of dehydrorotenone in a previous publication. It may be illustrated as follows:

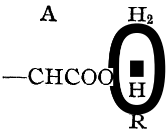


Rotenone Rotenolone Dehydrorotenone

(6) The cleavage of rotenone to derritol is best explained by the loss of the side ring from the nucleus by reduction in the manner indicated, although it seems strange that the double bond in the furan ring is not reduced by catalytic hydrogenation. However, this does not happen either with rotenone or with tubaic acid, and the fact must be due to the peculiar nature of the nucleus to which it is attached. (7) The cleavage of rotenone to tubaic acid is explained by the opening of the lactone



ring and hydrolysis or oxidation of the molecule at the carbonyl group. (8) The formation of an acid $C_{23}H_{26}O_6$ by catalytic reduction seems to be without analogy. The acid obtained by Butenandt is in all probability identical with dihydrorotenonic acid of this formula, which we have described in a previous article. Since many rotenone derivatives give analogous acids on hydrogenation, it will probably be found that as a rule any lactone containing the grouping A will react in a similar manner and give an acid on hydrogenation. In addition to the requirements postulated by Butenandt, all of which are fulfilled by the formula given by us, the derivatives of isorotenone still remain to be accounted for. These compounds are now being investigated.



A

Isorotenone is optically active but apparently does not contain a double bond easily reduced by hydrogen. It is easily obtained from rotenone by addition of hydrochloric acid to form rotenone hydrochloride, which in turn gives isorotenone with loss of hydrochloric acid. In a previous article[5] we have suggested that isorotenone does not contain a double bond but a ring structure instead. It seems likely that the iso-allyl group in the side chain has been converted into a trimethylene ring. Isorotenone gives isorotenol and isoderritol as well as dehydroisorotenone and dehydroisorotenonone, and has shown the typical reactions of rotenone in all our experiments, but further work on this derivative is necessary. It is to be expected that on energetic hydrogenation it would give isorotenonic acid, but not dihydro-isorotenonic acid. Dihydrorotenone should not give dihydro-isorotenone on boiling with sulfuric acid. Isorotenone should give isotubaic acid but, unlike tubaic acid, isotubaic acid on fusion with potassium hydroxide would probably not yield isorotenic acid. In other respects isorotenic acid should resemble tubaic acid, giving a phenol[6] with loss of the carboxyl group, and should exhibit similar color reactions. We are now investigating these points as well as the constitution of derric acid.

Summary

The typical reactions of rotenone are explained by a formula based on Takei's theory of the structures of rotenic, tubaic and dihydrotubaic acids, together with the composition and properties of derric acid.

The rotenone molecule is shown to consist of two parts joined together by a lactone and a ketone linkage. Rotenic acid is formed from one part, derric acid from the other.

WASHINGTON, D. C.

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[5] LaForge and Smith, THIS JOURNAL, 51, 2576 (1929).

[6] It is unfortunate that Takei has used the word "rotenol" to designate the phenol derived from rotenic acid because this word had already been used by Rutenandt to designate another compound.

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

A SULFUR ANALOG OF GLYCERIC ACID. BETA-THIOGLYCERIC ACID

BY C. FREDERICK KOELSCH

RECEIVED SEPTEMBER 27, 1929 PUBLISHED MARCH 6, 1930

In connection with a study of the oxidation–reduction relations of the sulfhydro group, a compound was needed whose molecule contained, in addition to the sulfhydro group, the carboxyl and hydroxyl groups. This paper describes the preparation of such a compound, β-thioglyceric acid.

Although the disulfide corresponding to this acid is formed by the action of nitrous acid on cystin[1] such a method appeared little suited to the preparation of a comparatively large quantity of the sulfhydro acid.

Several unsuccessful attempts were made to replace the halogen in sodium β-chlorolactate (a) with the sulfhydro group by treatment with sodium hydrosulfide or (b) with the xanthogeno group by treatment with potassium xanthate, according to well-known methods of preparation of mercapto acids.[2] The desired result was finally achieved by allowing ethyl β-chlorolactate to react with an alcoholic solution of potassium hydrosulfide, the resulting ethyl @-thioglycerate being subsequently hydrolyzed to the free acid.

Experimental

β-Chlorolactic Acid.—In a large glass cylinder having an internal diameter of about 5 cm. and fitted with a dropping funnel the lower end of which extended to within 2 mm. of the bottom of the cylinder, was placed a mixture of 250 g. of glycerol α-monochlorohydrin with 250 g. of water. In the dropping funnel was placed 350 g of nitric acid (sp. gr. 1.42). The nitric acid was allowed to flow into the chlorohydrin–water mixture in portions of about 20 ml., care being taken not to mix the layers formed. The addition was regulated so that there was always a layer of nitric acid at the bottom of the cylinder 5–10 mm. thick. A bright green color developed at the junction of the two layers, and slowly spread throughout the mixture. When all of the nitric acid had been added, which usually required two days, the mixture was allowed to stand until it had become colorless and no more oxides of nitrogen were evolved, requiring some six to eight days longer. (Several experiments designed to shorten the time necessary for the oxidation, in which the reaction mixture was warmed, with stirring, or in which a trace of vanadium pentoxide was added to the nitric acid resulted in the formation of a considerable amount of oxalic acid, with a consequent drop in the yield of β-chlorolactic acid.) The mixture was then transferred to a 1-liter Claisen flask and the water and most of the excess nitric acid were distilled off under reduced pressure (25–30 mm.) from

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[1] Neuberg and Ascher, *Biochem.* Z., 5, 451 (1907); Curtius and Kyriacou, *J. prakt. Cham.*, [2] 95, 360 (1917).

[2] (a) Klason and Carlson, *Ber.*, 39, 732 (1906); (b) Holmberg, *J. prakt. Chem.*, [2] *71*, 264 (1905); 75, 169 (1907); 88, 590 (1913); Biilman, *Ann.*, 339, 351 (1905); 348, 120 (1906); Biilmann and Madsen, *ibid.*, 402, 331 (1914).

a water-bath. The residue (230–240 g.), which became crystalline on standing, was pure enough for conversion into the ester. In one experiment the oxalic acid was removed by treating with precipitated calcium carbonate. The filtered solution of the calcium salt was mixed with a solution of slightly less than enough oxalic acid to precipitate all of the calcium, the calcium content being determined by analysis of an aliquot. After centrifuging off the calcium oxalate, the acid was extracted with ether. The sirupy residue left after the removal of the ether solidified on standing in a vacuum over sulfuric acid to a mass of thick needles melting at 70–75° and deliquescing on exposure to the air.

Anal. Subs., 0.1474; AgCl, 0.1742. Calcd. for $C_3H_5O_3Cl$: Cl, 28.5. Found: Cl, 29.2. *Neut. equiv.* Subs., 0.2222: 0.0995 *N* NaOH 17.3 ml. Mol. wt., calcd., 125.5. Found: 128.

For further purification the acid was crystallized from hot dry benzene, in which it is difficultly soluble. It separates from this solvent in clusters of fine needles melting at 77°.

Anal. Subs., 0.1884: AgCl, 0.2168. Found: Cl, 28.47.

The ammonium salt was prepared by dissolving 4 g. of the acid in 20 ml. of 95% alcohol, neutralizing with concd. aqueous ammonia, and adding 30 ml. of ether. On standing the solution deposited long thick needles melting, after washing with ether and drying in a vacuum over sulfuric acid, at 141° with decomposition.

Anal. Subs., 0.1797: AgCl, 0.1822. Calcd. for $C_3H_8O_3NCl$: Cl, 25.09. Found: Cl, 25.08.

Ethyl **β-Chlorolactate.**—Crude β-chlorolactic acid freed of water and nitric acid was dissolved in twice its weight of absolute alcohol containing 4% of hydrogen chloride and the solution was refluxed for four hours. The alcohol was distilled off from a water-bath, and the residue was distilled under reduced pressure. After two distillations the ester was obtained as an oil boiling at 106–108° at 25 mm. which soon solidified to a mass of colorless needles melting at 35–37°; yield, 80% of the weight of crude β-chlorolactic acid used.

Anal. Subs., 0.1694: AgCl, 0.1594. Calcd. for $C_5H_9O_3Cl$: Cl, 23.28. Found: Cl, 23.27.

Sodium **β-Chlorolactate** and Potassium **Xanthate.**—The reaction between these two substances was carried out in the usual manner. On acidification of the reaction mixture, an oil was precipitated which was identified as carbon bisulfide. Its weight, after purification, indicated that it represented 74% of the sulfur in the potassium xanthate used; the reaction mixture, which could contain at most only a small amount of the expected β-xanthogenolactic acid, was not investigated further.

β-Thioglyceric Ester, $CH_2SHCHOHCOOC_2H_5$.—A solution of 100 g. of potassium hydroxide in 560 ml. of 95% alcohol, contained in a I-liter 3-necked flask fitted with a stirrer and with a thermometer dipping into the liquid, was saturated at room temperature with hydrogen sulfide. To this was added about 20 ml. of a solution of 150 g. of ethyl β-chlorolactate in 185 ml. of alcohol. The mixture was warmed to 60–65°, at which temperature the reaction started, as was evidenced by the separation of potassium chloride. The temperature of the mixture was kept at 65–70° by the slow addition, with stirring, of the remainder of the ethyl β-chlorolactate solution. When the addition was completed, the mixture was heated at 70° with stirring for thirty minutes. The mixture was then cooled and dry hydrogen chloride was passed in until the mixture was acid to congo red. The potassium chloride was filtered off and the alcohol was distilled from the filtrate. The residue was distilled under reduced pressure, giving

33 g. of ethyl β-thioglycerate boiling at 113–115° at 19 mm.; d_{25}^{25} 1.1779; n_D^{25} 1.4754; R_m, calcd., 36.19; obs., 35.88.[3]

Anal.[4] Subs., 0.1799: 0.0917 N I_2 soln., 13.1 ml. Calcd. for $C_5H_{10}O_3S$: —SH, 22.0. Found: —SH, 22.0.

Along with the volatile β-thioglyceric ester, 71 g. of a thick oil was obtained which could not be distilled at 5 mm. It was analyzed for sulfur in the hope that this analysis would indicate whether it was principally β,β'-monothiodiglyceric ester or β,β'-dithiodiglyceric ester.

Anal. Subs., 0.2533: $BaSO_4$, 0.3200. Calcd. for $S(CH_2CHOHCOOC_2H_5)_2$, S, 12.0. Calcd. for $S_2(CH_2CHOHCOOC_2H_5)$: S, 21.4. Found: S, 17.36.

The substance showed no reducing properties toward iodine solution and was insoluble in dilute sodium hydroxide, It was not investigated further.

β-Thioglyceric Acid, $CH_2SHCHOHCOOH$.—To 300 ml. of 5% aqueous hydrochloric acid was added 32 g. of ethyl β-thioglycerate, and the mixture was refluxed for seven hours in an atmosphere of carbon dioxide. The solution was concentrated to a volume of about 60 ml. by distillation in a current of carbon dioxide and the residue was placed in a vacuum over sulfuric acid and potassium hydroxide. The sirup remaining after six days was analyzed.

Anal. Subs., 0.3228: 0.0917 N I_2 soln., 24.1 ml. Calcd. for $C_3H_6O_3S$: —SH, 26.2. Found: —SH, 22.6.

The acid decomposed when the distillation of a small quantity at 5 mm. was attempted. With ferric chloride in dilute aqueous solution the acid gives a transient blue color.

S-2,4-Dinitrophenyl-β-thioglyceric Acid, $(NO_2)_2C_6H_3SCH_2CHOHCOOH$.—Since the analysis of the mercapto acid obtained above agreed only approximately with that required by its formula, the S-2,4-dinitrophenyl ether was prepared and analyzed as a derivative characteristic of the sulfhydro group.[5] To a solution of 2.5 g. of β-thioglyceric acid in 70 ml. of 95% alcohol was added 10 g. of anhydrous sodium acetate. The mixture was boiled until most of the salt was dissolved, and the solution was filtered. To this solution was added 5 g. of 2,4-dinitrochlorobenzene. The mixture was boiled under a reflux for five minutes and then allowed to cool to room temperature. The crystalline sodium salt which separated was filtered off, washed with a little alcohol and dissolved in warm water. This solution was acidified with dilute sulfuric acid. The precipitate was filtered off and recrystallized twice from hot water. The acid was obtained thus in very small sulfur-yellow plates melting at 167–168° (uncorr.).

Anal. Subs., 0.2076: $BaSO_4$, 0.1685. Calcd. for $C_9H_8O_7N_2S$: S, 11.11. Found: S, 11.15. Neut. *equiv.* Subs.. 0.1503: 0.0802 N NaOH, 6.6 ml. Mol. wt., calcd., 288. Found: 284.

Barium β,β'-Dithiodiglycerate, $(—SCH_2CHOHCOO)_2Ba$.—A solution of 19 g. of β-thioglyceric acid in 100 ml. of water was made alkaline with a slight excess of ammonia. A slow current of oxygen was bubbled through the solution until a portion acidified with acetic acid no longer decolorized an aqueous iodine solution. The oxidation was complete in about ten hours. The solution was mixed with a concentrated solution of 20 g. of crystallized barium chloride and a slight turbidity which developed was filtered off. On mixing the solution with an equal volume of alcohol, the barium salt was precipitated

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[3] Value for atomic refraction of sulfur in C—S—H according to Price and Twiss, *J.* Chem. *Soc.*, 101, 1259 (1912).

[4] Klason and Carlson, Ber., 39, 738 (1906).

[5] Friedlander and Chwala, *Monatsh.*, 28,250 (1907).

as a white indistinctly crystalline powder. It was filtered off and allowed to stand in a vacuum over sulfuric acid overnight, when it changed to a thick sirup. This was dissolved in water and reprecipitated with alcohol. The precipitate was allowed to remain in contact with the mother liquor for two days, then filtered off and dried at 40° in air. The barium salt was obtained as a white chalky powder.

Anal. Subs., 0.1540, 0.1681: $BaSO_4$, 0.0943, 0.1034. Calcd. for $C_6H_8O_6S_2Ba$: Ba, 36.34. Found: Ba, 36.03, 36.19.

β,β'-Dithiodiglyceric Acid, $(-SCH_2CHOHCOOH)_2$.—A solution of 3.77 g. of the barium salt in water was treated with the calculated amount of *N* sulfuric acid. The barium sulfate was filtered off and the resulting solution was evaporated to a sirup on a water-bath. After this sirup had stood over sulfuric acid in a vacuum for several days, a thick gum remained, weighing 2.30 g. (calcd., 2.42 g.).

Anal. Subs., 0.1397: $BaSO_4$, 0.2676. Calcd. for $C_6H_{10}O_6S_2$: S, 26.45 Found: S, 26.31.

The acid was easily soluble in water and in ethyl acetate; it was precipitated from its solution in the latter solvent by chloroform as a sticky gum.

The writer wishes to express his appreciation of the assistance and advice offered by Professor S. M. McElvain.

Summary

1. A new method of preparation of β-chlorolactic acid has been described.

2. β-Thioglyceric acid and a few of its derivatives have been prepared from ethyl β-chlorolactate.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY AND THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

THE PREPARATION OF PRIMARY AMINES FROM ALDEHYDES AND MONOCHLORO-AMINE

BY CHARLES R. HAUSER

RECEIVED SEPTEMBER 30, 1929 PUBLISHED MARCH 6, 1930

In view of the fact that oximes have been reduced to primary amines, it would seem possible that chloro-imines could be reduced in a similar manner. Thus primary amines might be prepared from aldehydes and monochloro-amine by the reduction of the intermediate chloro-imine, as represented by the equation

$$RCH{=}O + H_2NCl \xrightarrow{-H_2O} RCH{=}NCl \xrightarrow{+\,4H} RCH_2NH_2HCl$$

With the exception of methylene chloro-imine,[1] apparently no chloro-imine prepared by this method has been isolated. However, there is evidence that benzalchloro-imine is the condensation product of benzaldehyde and monochloro-amine. Forster[2] reported that benzonitrile and

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[1] Cross, Bevan and Bacon, *J. Chem. Soc.*, 97, 2404 (1910).

[2] Forster, *ibid.*, 107, 265 (1915).

ammonium chloride are obtained when an ether solution of the supposed benzalchloro-imine is evaporated on a water-bath. Raschig[3] was unsuccessful in his attempt to purify the condensation product of benzaldehyde and monochloro-amine. His analysis of the crude product for active chlorine gave 80–85% of benzalchloro-imine, When heated with water or sodium hydroxide solution the condensation product decomposed into hydrogen chloride and benzonitrile.

In the present investigation no attempt was made to isolate the chloro-imines, as it seemed that these would be unstable in view of the fact that Luxmoore[4] has reported that pure benzalchloro-imine decomposes even at 0°. However, good yields of primary amines were obtained from certain aldehydes and monochloro-amine by reducing the intermediate chloro-imine in alcoholic solution with sodium amalgam. Further work on chloro-imines is being carried out.

Experimental

In a preliminary experiment further evidence was obtained that the condensation product of benzaldehyde and monochloro-amine is doubtless benzalchloro-imine. As would be expected[6] dry hydrogen chloride reacts with an ether or carbon tetrachloride solution of the condensation product according to the equation

$$RCH{=}NCl + 2HCl \longrightarrow RCH{=}NH{\cdot}HCl + Cl_2$$

The imine hydrochloride obtained as a white precipitate is readily hydrolyzed into benzaldehyde and ammonium chloride which were identified.

Monochloro-amine[6] in cold aqueous solution was condensed with three aromatic and two aliphatic aldehydes by a modification of the methods of Forster[2] and Raschig.[3] The crude condensation product was dissolved in alcohol and reduced with sodium amalgam by an adaptation of the method used by Goldschmidt[7] for the reduction of oximes. The results obtained with the aromatic aldehydes are given in Table I. The products obtained as amine hydrochlorides were analyzed and derivatives prepared.

Benzaldehyde and p-tolualdehyde gave yellow liquid condensation products doubtless mixed with some unchanged aldehyde, while o-chlorobenzaldehyde gave a white solid which melted to an oil at about 15–20". Analysis of the latter condensation product for the active chlorine showed that it was 90.2% pure calculated as the chloro-imine.

From each of the chloro-imines of benzaldehyde and o-chlorobenzaldehyde there

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[3] Raschig, "Schwefel- und Stickstoffstudien," 1924, p. 78.

[4] Luxmoore, *J. Chem. Soc.*, **69**, 191 (1896).

[5] Hydrogen chloride reacts with keto-chloro-imines to form the imine hydrochloride, Stieglitz and Peterson, *Ber.*, 43, 786 (1910).

[6] Monochloro-amine was prepared by the method of Coleman and Hauser, THIS JOURNAL, **50**, 1193 (1928). This is a modification of the method of Marckwald and Wille, *Ber.*. **56**, 1319 (1923).

[3] Goldschmidt, *ibid.*, **19**, 3232 (1888).

TABLE I

PERCENTAGE YIELDS

Aldehyde	*Condensation product*[m]	Amines (1)[b]	(2)[c]
p-$CH_3C_6H_4CHO$	69.0	63.6	43.8
C_6H_5CHO	70.2	73.5	51.5
o-ClC_6H_4CHO	87.7	77.0	67.5

[a] Yields of crude condensation products calculated from aldehydes. [b] Yields of primary amines calculated from crude condensation products. [c] Yields of primary amines calculated from aldehydes.

was obtained a yield of approximately 85% of primary amine calculated from the active chlorine content of the crude condensation product.

Two aliphatic aldehydes, n-propionaldehyde and n-butyraldehyde, gave with monochloro-amine fair yields of very unstable yellow liquids, which were assumed to be the crude chloro-imines. Since the reduction of these chloro-imines gave very small yields of amines, they were not studied farther in the present work.

Condensation of Aldehydes with **Monochloro-amine.**—The aldehyde was thoroughly shaken with excess of an ice-cold aqueous solution of monochloro-amine[6] prepared from equal volumes of normal solutions of sodium hypochlorite and ammonium hydroxide. Benzaldehyde, and likewise *p*-tolualdehyde, with monochloro-amine produced a milky mixture which was allowed to stand in an ice chest until the condensation product had settled to the bottom as a yellow oil. The condensation product was then separated, a weighed amount dissolved in alcohol and reduced as described below. A milky mixture was at first produced from o-chlorobenzaldehyde and monochloro-amine, but after shaking for about fifteen minutes a white precipitate formed. The precipitate was filtered off at a low temperature and a weighed amount dissolved in alcohol and reduced. In these reactions sufficient monochloro-amine solution was always used to have its odor persist until the condensation product was separated from the aqueous solution.

Reduction—Approximately twice the theoretical amount of sodium amalgam (2.5%) was added in small portions to a solution of 2 g. of the crude condensation product in 25 cc. of alcohol and 12 cc. of glacial acetic acid. The reaction mixture was kept below 35°. More alcohol was added if a heavy precipitate formed. When the reaction was complete three volumes of water were added, and after separating the mercury the cooled solution was made alkaline. The aqueous solution of amine was extracted three times with ether and the ether solution extracted with dilute hydrochloric acid. The amine hydrochloride, obtained by evaporating the hydrochloric acid solution on a water-bath, was dried thoroughly in'a vacuum desiccator.

The purity of the amine hydrochlorides was determined by analysis and the amines were identified by preparing derivatives and taking mixed melting points when known compounds were available.

Anal. Calcd. for $C_8H_{11}N\cdot HCl$: N, 8.89; HCl, 23.16. Found: N, 8.77; HCl, 23.20.

Anal. Calcd. for $C_7H_9N\cdot HCl$: N, 9.76; HCl, 25.51. Found: N, 9.89; HCl, 25.15.

Anal. Calcd. for $C_7H_8NCl\cdot HCl$: N, 7.87; HCl, 20.50. Found: N, 7.86; HCl, 20.40.

Several reductions of benzalchloro-imine were carried out at temperatures ranging from 0 to 40° and it was found that below 35" approximately the same yields of amines were obtained. A smaller yield was obtained when the reaction was carried out at 30–40° by adding the acetic acid slowly so that the solution was always slightly acidic.

Summary

A method for the preparation of certain primary amines is described in which monochloro-amine is condensed with an aldehyde and the condensation product in alcoholic solution reduced with sodium amalgam.

DURHAM, NORTH CAROLINA

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

THE THERMAL DECOMPOSITION OF METAL ALKYLS IN HYDROGEN–ETHYLENE MIXTURES

BY HUGH S. TAYLOR AND WILLIAM H. JONES

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The reactivity of metal alkyls undergoing decomposition by heat offers many interesting problems of both scientific and practical interest. The production of a reactive fragment of decomposition among inert hydrocarbons might offer a means of bringing these compounds into a state of reactivity with the possible formation of more interesting products. A study of the reactivity of such fragments with hydrogen is of importance also as indicating the direction of chemical change in systems obtaining when hydrocarbons are subjected to processes of thermal degradation or "cracking." To these ends we have investigated the decomposition of several metal alkyls in the presence of various mixtures of hydrogen and ethylene.

When a metal alkyl is decomposed by heat, leaving the free metal as a deposit, it seems an unavoidable assumption that the alkyl group must have existed, at least for a short space of time, as a free radical. If it can then be shown that any resulting reaction could not be attributed to the metal or to the temperature, the postulated mechanism of whatever reaction occurs must be such as to involve the alkyl radical. For this reason mercury diethyl and lead tetraethyl were chosen, since they decompose under temperature conditions which do not of themselves induce reaction of hydrogen and ethylene, and since the metals themselves do not exhibit any marked catalytic effect.

Extensive recent work by Taylor and Marshall,[1] Olson and Meyers,[2] Bates and Taylor,[3] Taylor and Hill,[4] Bonhoeffer and Harteck,[5] von Wartenburg and Schultze,[6] and others demonstrates the interest which atomic

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[1] Taylor and Marshall, *J. Phys. Chem.*, **29**, 1140 (1925).

[2] Olson and Meyers, THIS JOURNAL, 48,389 (1926).

[3] Bates and Taylor, *ibid.*, **49**, 2438 (1927).

[4] Taylor and Hill (Taylor, "Nichols Medal Address"), *Ind. Eng. Chem.*, *20*, 439 (1928); THIS JOURNAL, 51, 2922 (1929).

[5] Bonhoeffer and Harteck, Z. *physik. Chem.*, **139A**, 64 (1928).

[6] Von Wartenburg and Schultze, *ibid.*, **2B**, 1 (1929).

hydrogen and its reaction with hydrocarbons have aroused. Taylor postulated the formation of ethyl radicals by interaction of hydrogen atoms and ethylene, and examined from the energetic standpoint the possible production of ethane from ethyl radicals and hydrogen molecules. The decomposition of mercury diethyl might yield ethyl radicals direct and thus might induce ethane formation in a hydrogen atmosphere. In this paper it is shown that the liberation of ethyl radicals in a mixture of hydrogen and ethylene produces the same results as does the introduction of hydrogen atoms. It will be shown that the product is mainly a polymeric form of ethylene without considerable quantities of saturated hydrocarbons, and that the ultimate products from atomic hydrogen and hydrocarbons are similar. This points to similar stages in the two sets of reactions.

The literature offers only slight data as to the products of thermal decomposition of the metal alkyls.[7] Evidence as to these products may be derived from any reaction they cause in a hydrogen–ethylene mixture, or from a blank run using the metal alkyl alone. Moreover, since mercury diethyl and lead tetra-ethyl were the compounds used, the investigation of their thermal decomposition in hydrocarbon–hydrogen mixtures might serve to throw some light on their anti-knock action in motor fuels, since in that case they are thermally decomposed in a hydrocarbon–air mixture.

Experimental Details

Apparatus.—The apparatus was set up as shown in Fig. 1. It was made of soft glass without rubber joints, and all connecting parts were of capillary tubing. The reaction chamber A was of 250 cc. capacity, made of pyrex with capillary side tube and ground joint C for connecting to the remainder of the apparatus. The reaction chamber was closed with a ground-glass stopper B, and an inlet and exit tube were provided for circulating water through the body of the stopper itself. A resistance furnace F, which could be raised and clamped about the reaction chamber, was used to maintain it at 250 to 300°. The furnace was not considerably larger than the reaction vessel. Consequently a certain temperature gradient existed along the tube, hottest in the middle and cooler toward each end. The gradient was, however, always within the limits stated, 250–300°. D is an open-tube mercury manometer, and E is a precision gas buret, water-jacketed and using mercury for the containing liquid. The mercury compensating arm of the buret had platinum leads sealed through, and connection was made through a small lamp to a battery, to give reproducibility in readings. The manometer was similarly arranged. From the other arm of the three-way stopcock on the buret, passage was provided through suitable stopcocks to a pump, to the outer air, and to a gas analysis apparatus. This latter was of the Orsat type, with mercury-filled water-jacketed precision buret similar to E, and connecting by a branching capillary to four liquid absorption pipets of the bubbling type containing, respectively, potassium hydroxide solution, fuming sulfuric acid, alkaline pyrogallol and acid cuprous chloride. The fifth outlet carried a pipet with sealed-in platinum spiral for

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[7] Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, 1921, p. 92.

slow combustion, and the sixth a tube of copper oxide, both using mercury as the containing fluid. The copper oxide tube was constantly maintained at 250–280° by a wrapping of resistance wire connected to a transformer.

Preparation of Materials.—The mercury diethyl and mercury dimethyl were prepared by several methods, the most satisfactory being that of Marvel and Gould.[8] Both were found to boil sharply, after being twice distilled, the diethyl at 97–99° under 125 mm. pressure and the dimethyl at 94° and atmospheric pressure. One sample of mercury diethyl was lost when it decomposed with a slight explosion during distillation, leaving distilling flask, fractionating column and condenser coated with a gray deposit of mercury. One sample of mercury dimethyl was kindly furnished by Professor Marvel, while all of the lead tetra-ethyl used in this work was the product of the E. I. du Pont de Nemours Company. The hydrogen was electrolytic hydrogen taken from cylinders, and was purified by passing first over heated platinized asbestos and then over phosphorus pentoxide. The ethylene was taken from a cylinder of the commercial gas, the quality of which has frequently been tested in this Laboratory for catalytic purposes with completely satisfactory results.[9] It was passed over phosphorus pentoxide before use.

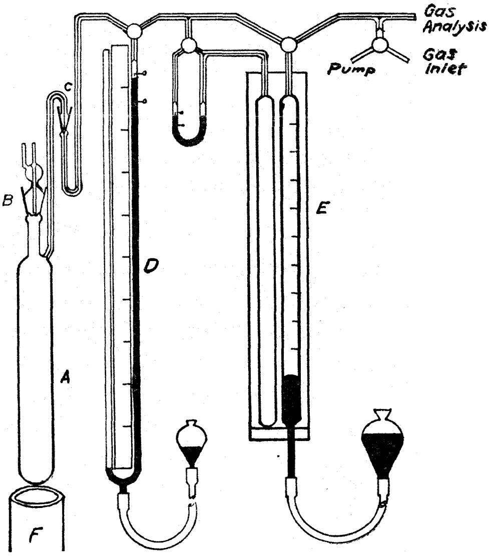

Fig. 1.

Experimental Procedure

In making a run the reaction tube was unsealed at B and C and a small sealed thin-walled bulb containing a known weight of the metal alkyl was introduced. The reaction vessel was then reattached, using de Khotinsky cement on top of the ground-glass joints, which were water-cooled, and the entire apparatus evacuated. The apparatus was always washed out several times by admitting and pumping out one of the gases to be used in the run, usually hydrogen. For the actual run, each portion of gas admitted was measured through the buret and then transferred to the reaction chamber. Finally the manometer was read and the furnace clamped in position and turned on, having previously been adjusted for a temperature of 250–300°. There was, obviously, first of all an increase in pressure due to the rise in temperature, followed by a further sudden increase when the bulb of alkyl burst. A maximum pressure was then developed followed by a reduction in pressure due to reaction. In most cases there was no further volume change after five to seven hours. It is evident that we chose a temperature range in which the decomposition of alkyl was a slow reaction. In this temperature range the rate of decomposition of mercury diethyl was much faster than that of dimethyl, which latter also showed considerable tendency to distillation without decomposition to the cooler parts of the reaction system. It is for this reason

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[8] Marvel and Gould, THIS JOURNAL, 44, 153 (1922).

[9] Pease, ibid., 45, 1196 (1923).

that its use was abandoned. It should be observed that the rates of decomposition of the **alkyls** under these dilute conditions are radically different from those obtaining during bulk distillations of the material.

On attainment of constant pressure the heat was removed, and when cool a final reading of the pressure and temperature was taken. **A** sample of the gas was then withdrawn, using the buret E as a pump, and passed directly into the buret of the gas analysis apparatus, where its composition was determined.

In each of the first eight runs the apparatus was immediately evacuated without being disconnected and the experiment was followed by a blank run, using the same gases in approximately the same quantities as before, in order to determine whether the results could in any degree be attributed to catalytic effects of the free metal resulting from the decomposition of the metal alkyl. As every case showed no volume change after prolonged heating, this practice was discontinued.

Experimental Results

The results of the runs made are presented in the two tables herewith shown. No run using a metal alkyl alone, or with hydrogen or ethylene, or both, has been omitted. Table I presents in columns two and three the volumes of reacting gases introduced. In the fourth column the weight and nature of the metal alkyl is given, and this is calculated to the number of cubic centimeters of free alkyl radicals that would be liberated on complete decomposition, giving the values recorded in the fifth column. The sixth column shows the volume after reaction, as calculated from the original volume and the original and final manometer readings. The subsequent analysis showed how much of this volume was

TABLE I

EXPERIMENTAL RESULTS

All gas volumes in a given experiment are calculated to the same temperature and pressure.

Expt.	H_2 taken, cc.	C_2H_4 taken, cc.	Metal alkyl, g.	C_2H_5 equiv., cc.	Vol. after reaction	*He* dis-appeared, cc.	C_2H_4 disap-peared, cc.	*Ce* as satd. gas	C_2 as liquid
1	46.6	44.4	0.105"	19.2	60.4		13		
2	49.2	49.6	.316^a	57.8	89.4		33.9		
3	50.4	50 1	.023^a	4.2	84.7	11 65	19.5		
4	None	95.9	.249^a	45.5	50.0		80.3		
5	51.0	50.4	.209^b	57.8	96.5	13.0	33.8		
6	50.2	50.8	.388^c	79.8	93.9				
7	49.8	50.5	.0301^a	5.5	85.3				
8	53.1	47.9	,0176"	3.2	98.4				
9	None	None	.0904^c	18.8	2.6				
10	None	None	.2844^c	59.3	10.5				
11	None	None	.4416^c	92.0	38.2				
12	None	None	.3930^a	36.0	24.8	−0.7	−5.2	7.6	23.2
13	None	84.2	,0316"	5.8	78.7	−1.4	8.4	Lost	Lost
14	None	95.9	.0186^a	3.4	77.4	0.0	22.3	6.4	19.3
15	49.4	493	.0359^a	6.6	80.7	5.2	19.1	17.1	8.6
16	56.0	54.8	.0672^a	12.3	88.5	12.1	28.9	6.4	34.8
17	50.5	47.5	.0692^a	12.7	80.4	4.0	24.8	5.6	31.9
18	61.4	64.0	.0480^a	8.8	99.7	5.4	28.3	11.9	25.2

TABLE I *(Concluded)*

Expt.	H_2 taken, cc.	C_2H_4 taken, cc.	Metal alkyl, g.	C_2H_5 equiv., cc.	Vol. after reaction	H_2 disappeared, cc.	C_2H_4 disappeared, cc.	C_2 as satd. gas	C_2 as liquid
19	64.1	31.4	0.0615[a]	11.3	81.1	6.7	18.5	Lost	Lost
20	69.2	29.5	.0319[a]	5.8	87.4	6.2	12.6	15.3	3.f
21	68.6	17.9	.0389[a]	7.1	77.3	6.6	13.4	4.3	16.2
22	83.1	None	.0870[a]	15.9	92.2	6.9		17.7	−1.8
23	25.1	69.5	.0212[a]	3.9	79.7	−1.7	17.9	4.0	17.8
24	50.3	49.6	.0427[a]	8.1	83.1	4.8	19.7	6.5	21.3
25[d]	50.5	51.3	.0359[a]	6.9	85.3	3.1	20.3	5.8	21.4
26	92.0	92.0	.1092[a]	20.8	164.7	−8.0	32.7	10.6	42.9
27	95.1	98.1	.0668[a]	12.8	157.7	7.7	38.8	9.6	42.0
28	22.9	24.7	.0393[a]	7.5	42.5	4.0	8.4	6.1	9.8
29	52.8	52.0	.0336[b]	103	88.3	7.9	22.1	5.4	27.0
30	92.2	95.4	.0308[b]	9.2	161.1	7.1	30.5	7.0	32.7
31	29.7	29.4	.0174[b]	5.2	50.8	1.5	11.0	4.3	11.9
32	67.9	34.2	.0216[b]	6.7	90.3	10.6	16.6	5.3	18.0
33	325	66.1	.0262[b]	8.0	79.3	1.8	23.5	5.9	25.6
34	51.9	52.8	.0348[b]	10.6	93.9	3.6	14.5	5.3	19.8
35	51.0	50.4	.0356[b]	10.9	91.8	1.7	13.6	5.0	19.5

[a] $Hg(C_2H_5)_2$. [b] $Pb(C_2H_5)_4$. [c] $Hg(CH_3)_2$. [d] Run No. 25 was made using the reaction chamber filled with glass wool.

TABLE II
EXPERIMENTAL RESULTS

Run	Before reaction Gas, cc. H_2	Before reaction Gas, cc. C_2H_4	Before reaction Liquid C_2H_5, cc.	After reaction Gas, cc. H_2	After reaction Gas, cc. C_2H_4	After reaction Saturated	After reaction Liquid, cc. H_2	After reaction Liquid, cc. C_2
12	..	..	36.0	0.7	5.2	$18.9C_{0.8}$[a]	44.9	23.2
14	..	95.9	3.4	None	73.6	$3.7C_{3.46}$	36.6	19.3
15	49.4	49.3	6.6	44.2	30.2	$6.3C_{5.43}$	19.4	8.6
16	56.0	54.8	12.3	43.9	25.9	$18.7C_{0.68}$[a]	69.15	34.8
17	50.5	47.5	12.7	46.5	22.7	$11.2C_1$	62.95	31.9
18	61.4	64.0	8.8	56.0	35.7	$8C_{2.97}$	52.2	25.2
20	69.2	29.5	5.8	63.0	16.9	$7.5C_4$	7.8	3.1
21	68.6	17.9	7.1	62.0	4.5	$10.8C_{0.8}$[a]	31.8	16.2
23	25.1	69.5	3.9	26.8	51.6	$1.3C_6$	34.7	17.8
24	50.3	49.6	8.1	45.5	29.9	$7.7C_{1.69}$	43.7	21.3
25	50.5	51.3	6.9	47.4	31.0	$6.9C_{1.7}$	42.3	21.4
26	92.0	92.0	20.8	100.0	59.3	$5.4C_4$	82.9	42.9
27	95.1	98.1	12.8	87.4	59.3	$11.0C_{1.75}$	87.0	42.0
28	22.9	24.7	7.5	18.9	16.3	$7.3C_{1.67}$	20.0	9.8
29	52.8	52.0	10.3	44.9	29.9	$13.5C_{0.8}$[a]	53.5	27.0
30	92.2	95.4	9.2	85.1	64.9	$11.1C_{1.26}$	66.0	32.7
31	29.7	29.4	5.2	28.2	18.4	$4.3C_2$	23.6	11.9
32	67.9	34.2	6.7	57.3	17.6	$15.4C_{0.7}$[a]	34.3	18.0
33	32.5	66.1	8.0	30.7	42.6	$6.0C_{1.97}$	51.0	25.6
34	51.9	52.8	10.6	48.3	38.3	$7.3C_{1.44}$	41.2	19.8
35	51.0	50.4	10.9	49.3	36.8	$5.7C_{1.76}$	40.4	19.5

[a] The low values for carbon content are undoubtedly due to imperfect removal of hydrogen in the copper oxide. We have satisfied ourselves that this in no way affects the validity of our conclusions concerning the carbon–hydrogen balance.

ethylene (or other unsaturated gases) and how much hydrogen, and these values subtracted from the volumes introduced give the values which comprise the seventh and eighth columns.

In the first nine runs the analysis was made by cooling the tip of the reaction tube in liquid air, and assuming that the uncondensed gas was hydrogen. It was then warmed to room temperature and a part drawn off into a bromine pipet to determine the percentage of unsaturated hydrocarbons. In Runs 9, 10 and 11 the volume of gas after reaction was too small to be so analyzed. Since it was necessary to know more about the residual gas, the Orsat gas apparatus was sealed on at this time and used in all subsequent runs. The accuracy thus achieved permitted the calculation of the last two columns. Since it was not known what molecular formula could be assigned to the saturated hydrocarbons remaining after the removal of all other constituents, they are reported in the eighth column as cubic centimeters of C_2, that is, half the volume of carbon dioxide formed on combustion. Knowing then the amount of C_2 introduced and the amount appearing in the gas phase after the reaction, the difference gives the amount of C_2 transformed into liquid, that is, the volume of ethylene converted into liquid products.

It remained to be shown, however, what was the nature of the liquid. For this purpose the second table was compiled. In it the first six columns are derived from the corresponding columns of Table I. The seventh column gives the number of cubic centimeters of saturated hydrocarbon present after the reaction (residual volume less the volumes of ethylene and hydrogen found) and its mean carbon content. The calculation of this latter can best be shown by an example. In Run 14 the volume of saturated gas was 3.7 cc., which when burned gave 12.8 cc. of carbon dioxide (twice the value in column ten of Table I). It must then consist of a mixture of hydrocarbons, and the mean carbon content of the mixture must be 12.8/3.7, or $C_{3.46}$. Since the general formula is $C_nH_{2n} + 2$ and in this case $n = 3.46$, the H_2 content of the 3.7 cc. of saturated hydrocarbon is 16.4 cc. Knowing this, the difference between the volume of H_2 introduced (in all forms) and the volume of H_2 in the gas phase after the reaction

$$(H_2 + 2C_2H_4 + 2^1/_2C_2H_5) \longrightarrow (H_2 + 2C_2H_4 + H_2 \text{ as satd.})$$

gives the H_2 content of the liquid, which is shown in column eight. Column ten of Table I, the C content of the liquid, is brought down as column nine of Table II, this giving the H_2 and C_2 content of the liquid in adjacent columns. From comparison of these values, it is at once evident that within the experimental error the formula for the liquid is C_nH_{2n}, that is, it is a polymer of ethylene.

Dynamic Run.--Since it was evident that a considerable portion of the products of reaction were liquids, an apparatus was set up for a dynamic run. In this apparatus

(Fig. 2) hydrogen, having passed through platinized asbestos and phosphorus pentoxide, joined a stream of ethylene dried by phosphorus pentoxide. Each gas was measured through a calibrated flowmeter and the combined stream could then pass directly into the furnace or could be forced through a by-pass where it bubbled through a triple-effect wash bottle containing lead tetra-ethyl. The reaction chamber consisted of a piece of forty-millimeter tubing in the line, about which was a resistance furnace for maintaining a working temperature of 310–350°. The reaction tube was filled with glass wool to break up the stream of gas and produce more uniform heating. The gas leaving the furnace passed through two traps cooled by carbon dioxide--ether mixture for removing condensable products.

Two runs, each preceded by a blank, were made using this apparatus. The first blank was made by passing ethylene through the furnace at 325°, which gave no condensable product. The first run was then made by turning the stopcock to force the gas to pass through the lead tetra-ethyl before entering the furnace. In this case a liquid collected in the trap. The trap was then cut off and allowed to warm to room temperature. As it warmed, the gas it gave off between 12 and 30° was passed into a gas buret. Its volume was 83.5 cc., and the bromine pipet showed it to be 80% unsaturated. This could not have been mainly ethylene or propylene, since the gas analyzed was caught only above —12".

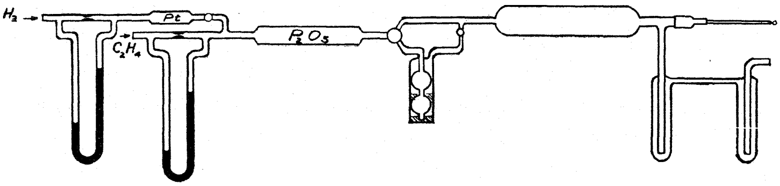

Fig. 2.

The trap containing the liquid was then transferred to a sulfuric acid bath and heated in an effort to determine the boiling point of the liquid. At 150° no boiling occurred, though the liquid was vaporizing rather rapidly at that temperature, as could be seen by the presence of a condensation zone about two centimeters above the surface of the acid, where the vapors condensed and flowed back in a film on the wall.

A second dynamic run was made using hydrogen and ethylene. In a preliminary blank run these gases were passed through the furnace at 310–250° without metal alkyl, and gave no product condensable by carbon dioxide–ether. The by-pass through the lead tetra-ethyl was then used, and the products began to collect in the trap. The flowmeters indicated that the entering gas was 42% ethylene when a sample of the gas issuing from the final trap was passed into the gas buret. A bromination on this sample showed it to consist of 36% of unsaturates. The liquid collecting in the trap was seen to contain suspended flakes of a white solid. If the cooling liquid was removed for a short time, the solid dissolved in the liquid, and was reprecipitated when the trap was again cooled. When the run was stopped, the trap was cut off and placed in a sulfuric acid bath. Its contents were found to boil when the thermometer in the acid read 75".

Discussion of Results

Decomposition Products from Alkyl Alone.—In Run 12, the first using the Orsat apparatus, a bulb containing 0.3930 *g.* of mercury diethyl—enough to furnish 36 cc. of ethyl groups at room temperature and pressure—was introduced and the contents decomposed by heat in the absence of other gases. When the decomposition products were analyzed and the composition of the liquid was calculated, it was found that 80% of the carbon and hydrogen appearing in the end-products did so as unsaturated substances. This confirms the statement[7] that the reaction is not the simple formation of butane which one might first expect according to the equation

$$Hg(C_2H_5)_2 = Hg + C_4H_{10}$$

but is rather a complicated one resulting in a mixture of hydrocarbons, both liquid and gas. In the gas phase saturated compounds predominate, while the liquid is a polymer of ethylene, since the calculation of the composition of the latter shows it to be C_nH_{2n} within the limits of experimental error, any deviation from this ratio being rather on the side of the acetylene than of the methane series.

Induced Polymerization.—If we assume that the original decomposition products are ethyl groups, it is evident that their liberation into an atmosphere of ethylene alone induces the latter to polymerize, as is demonstrated by all of the experiments and by Expt. 14 in particular. Here 0.0186 g. of mercury diethyl was used, representing only 3.4 cc. of ethyl radicals. At the end of the run, however, 19.3 cubic centimeters of ethylene was shown to be in the form of a liquid polymer. This shows conclusively that the ethyl groups have brought about an amount of polymerization disproportionate to their own volume. Nor does the presence of hydrogen prevent this from being the case, for in Expt. 33 it is shown that 6.7 cc. of ethyl radicals caused the polymerization of 18.0 cc. of ethylene, despite the fact that there was twice as much hydrogen as ethylene in the original mixture.

Extent of Hydrogenation.—It is evident that hydrogenation of the ethylene does not occur to a major extent, but the amount of hydrogenation does increase with the ratio of hydrogen admixed. To demonstrate this, runs were made with varying ratios of hydrogen and ethylene. In Expt. 33, for instance, hydrogen was present in half as great volume as ethylene, in Expt. 35 the volumes were equal, and in Expt. 32 there was twice as much hydrogen as ethylene, the total volume in each case being approximately 100 cc. The results show that the amount of liquid polymer formed increases with the volume of ethylene in the original mixture, though the relation is not at all linear.

Effect of Pressure.—A series of runs was also made to investigate the effect of pressure. In these runs the hydrogen and ethylene were introduced in nearly equal quantities, but the total volume was about 50 cc. in Expt. 28, about 100 cc. in Expt. 35, and about 185 cc. in Expt. 26. When the amounts of ethylene polymerized in each case are considered, the degree of polymerization is found to be roughly proportional to the pressure, since the value for each in the last column of either table is 9.8, 19.5 and 43.0 cc., respectively.

Effect of Alkyl Concentration and Nature of the Metal.—A comparison of values of ethylene polymerized and ethyl radicals taken will also show that when more ethyl groups are used, more polymerization is accomplished, other things being equal. When mercury diethyl was replaced by lead tetra-ethyl, no change was observed that could be attributed to the difference in the metallic element of the compound.

Wall Effect.—Experiment 25 was made with the reaction chamber filled with glass wool. When it is compared with others, as for example Expt. 24, it is seen that the results are in close agreement. This indicates that a wall effect is not involved to any important extent; the reaction appears to occur in the gas phase. Certain recent considerations of Bonhoeffer and Harteck[6] indicate that the addition of hydrogen atoms to ethylene may possibly be a wall reaction. There is no evidence of such in our work but this may be because we are dealing essentially with a polymerization process. Some recent work of Pease and Chesebro[10] shows that the thermal polymerizations of ethylene and acetylene in glass vessels are essentially homogeneous gaseous reactions.

Discussion of Mechanism

The outstanding result experimentally is the induced polymerization of ethylene by the decomposition of the metal alkyl under conditions of temperature at which ethylene will not polymerize of itself. Any proposed mechanism must suggest a method whereby this may be accomplished. At the same time, it is to be noted that a certain amount of saturated hydrocarbons is produced even in the absence of hydrogen initially. With two exceptions (Expts. 15 and 20), in all experiments in which hydrogen and ethylene are initially present, the polymerized product is greatly in excess of the saturated product. In Expt. 20 the reason for the exception apparently lies in the excess of initial hydrogen, since in Expt. 22 where no ethylene was initially present practically the whole of the alkyl decomposition product appears as saturated hydrocarbon in contrast to the relatively large amounts of unsaturated product in Expts. 12, 13 and 14, where there was no hydrogen originally present. This indicates that the reactivity of the decomposition product of metal alkyl with ethylene is much more pronounced than with hydrogen. Our experiments with several ratios of the gases confirm this.

We shall assume that the decomposition of the ethyl compounds yields initially free ethyl radicals, whether from mercury or lead

$$Hg(C_2H_5)_2 = Hg + 2C_2H_5 \qquad (1)$$

Since, according to modern concepts, the direct addition of two mole-

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[10] Pease and Chesebro, *Proc. Nat. Acad. Sci.*, 14,472 (1928).

cules to form a single molecule in the gas phase is an improbable event, we must assume that the process building up hydrocarbon chains does not proceed by a bimolecular reaction of the type

$$C_2H_5 + C_2H_4 = C_4H_9$$

but rather as a three-body collision

$$C_2H_5 + C_2H_4 + C_2H_4 = C_4H_9 + C_2H_4 \qquad (2)$$

an addition of ethylene which may repeat itself, also by a three-body collision

$$C_4H_9 + C_2H_4 + C_2H_4 = C_6H_{13} + C_2H_4 \qquad (3)$$

All such reactions, however, result in free radicals, whereas we have to account for the production of unsaturated polymer $(CH_2)_n$ and saturated product of varying complexity. We can offer several alternative methods whereby these may be produced. Thus, the collision of two radicals may produce one saturated and one unsaturated hydrocarbon, for example

$$C_6H_{13} + C_2H_5 = C_2H_6 + C_6H_{12} + 54 \text{ Cal.} \qquad (4)$$

Since, in general, the C_2 appearing as unsaturated is upward of three times the C_2 appearing as saturated, it is evident that Reaction 4 would represent the simplest process yielding the ratio of $3C_2$ unsaturated to C_2 saturated. Greater ratios would demand further reactions of the type in (2) and (3) prior to the reaction typified by (4). One objection to such a sequence is that reactions of the type in (2) and (3) ought to be greatly in excess of that in (4) since this latter involves reaction between two radicals present only in minute quantities.

This objection can be avoided if we postulate another method whereby a liquid unsaturated polymer may be produced. After processes of the type indicated in (2) and (3) have proceeded, it is possible that they may be succeeded by a reaction of a new type exemplified by the equation

$$C_6H_{13} + C_2H_4 = C_6H_{12} + C_2H_5 + 0 \text{ Cal.} \qquad (5)$$

There is little objection to such a reaction either on the basis of collision frequency or from the energetic standpoint. The reaction would occur more readily the higher the molecular weight of the radical involved. It will be noted that the reaction involves the reproduction of the ethyl radical and hence the possibility of a chain of reactions. Such a chain of reactions could be stopped in various ways. Reaction 4 represents one method. Clean-up on the walls of the containing vessel followed by reaction there, possibly of Type 4, also would form one other method. Interaction with hydrogen which evidently occurs, as is to be concluded from the hydrogen disappearance, represents another method. The precise mechanism of these latter reactions is somewhat uncertain since, as pointed out by Bonhoeffer and Harteck,[5] the reaction

$$C_2H_5 + H_2 = C_2H_6 + H - 10 \text{ Cal.} \qquad (6)$$

should be endothermic. There is, however, another alternative, namely

$$C_2H_5 + H_2 = CH_4 + CH_3 + 30 \text{ Cal.} \qquad (7)$$

which is energetically possible and would account for the methane which we have found in our saturated gas. The final elimination of free radicals must in these cases also be either by (4) or by wall reactions.

A detailed study of the reaction between excited mercury, hydrogen and ethylene, recently completed by Taylor and Hill,[11] has shown that so far as end-products are concerned there is complete parallelism between the alkyl decomposition reaction and that with excited mercury. We are satisfied also that the reactions discussed above may be harmonized with those possible when the starting point is atomic hydrogen rather than a metal alkyl fragment.

The results are indeed highly reminiscent of those of Lind[12] and his co-workers[13] from the interaction of a-particles with ethylene and saturated hydrocarbons. In all these studies it is evident that a polymer $(CH_2)_n$ is the principal product. In the present experiments, there can be no question of ionization occurring; also the amount polymerized bears somewhat the same ratio to activating agent (about 6:1) that is found by Lind for the M/N ratio in ethylene. The question at once suggests itself as to whether it is necessary in the a-particle experiment to assume clustering around ions or whether one should not assume the formation of radicals as a resultant of the action of the a-particles followed by a sequence of chemical processes identical with those obtaining as a result of the introduction to such systems of either atomic hydrogen or, as in our experiments, free radicals.

Summary

1. It has been shown that the ultimate products of thermal decomposition of mercury diethyl are both gaseous and liquid, and are for the most part unsaturated in nature.

2. Polymerization of ethylene induced by decomposing mercury diethyl in an atmosphere of ethylene has been observed, and the polyethylenic nature of the polymer demonstrated.

3. The decomposition of mercury diethyl in a mixture of hydrogen and ethylene has been found to produce mainly an ethylene polymer in addition to a small amount of saturated hydrocarbons.

4. The effects of alkyl concentration, gas ratio, pressure, containing wall and nature of the metal alkyl have been studied.

5. Using a flow method a liquid product, $(CH_2)_n$, was collected and some of its properties were observed.

6. A possible mechanism for the formation of higher unsaturated and saturated hydrocarbons involving ethyl radicals has been offered.

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[11] Taylor and Hill, THIS JOURNAL, 51,2922 (1929).

[12] Lind, Bardwell and Perry, *ibid.*, 48, 1556 (1926).

[13] Lind and Bardwell, *ibid.*, 48,2335 (1926).

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

A NEW CYCLIC AZOXY COMPOUND

By S. C. Hussey, C. S. Marvel and F. D. Hager

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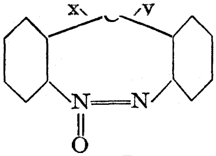
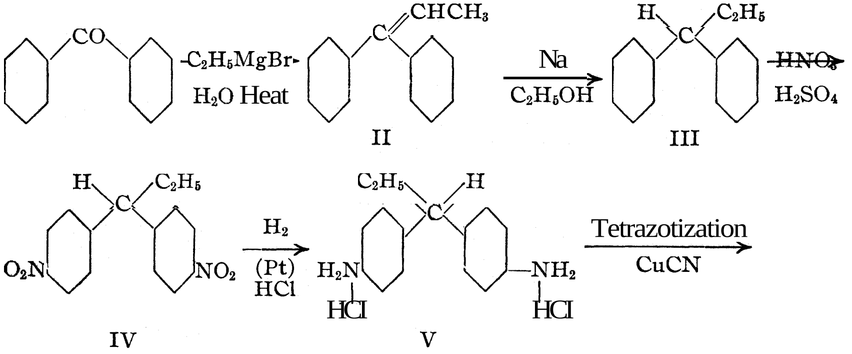
The work of Angeli[1] has left very little question concerning the unsymmetrical structure of the azoxy grouping. However, if a molecule of the type indicated in Formula I could be prepared and resolved it would furnish a new kind of evidence to confirm the views of Angeli. The present communication describes some experiments in which such a molecule has been prepared.



I

Very few compounds have been described in which the azoxy group is part of a ring system. Tauber[2] and later Ullmann and Dieterle[3] have prepared o,o′-azoxydiphenyl by the reduction of *o,o′*-dinitrodiphenyl. Duval[4] and later King[6] have prepared 2,2′-azoxy-4,4′-diaminodiphenylmethane by reduction of the corresponding dinitro compound. Duval[6] has also prepared 2,2′-azoxydiphenylmethane-4,4′-dicarboxylic acid and its diethyl ester by the same general method.

In some preliminary work attempts were made to nitrate benzilic acid to the *o,o′*-dinitro derivative. However, these were unsuccessful. An attempt to obtain 2,2′-dinitro-4,4′-diaminodiphenylcarbinol by the oxidation of the methane derivative was also unsuccessful. The following synthesis starting with benzophenone was finally accomplished.



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[1] A summary of Angeli's work is given in *Ahren's Sammlung Chem. und Chem. tech. Vortrage*, **19**,**447** (1913), and also in *Gazz. chim. ital.*, **46**, II, 67 (1916).

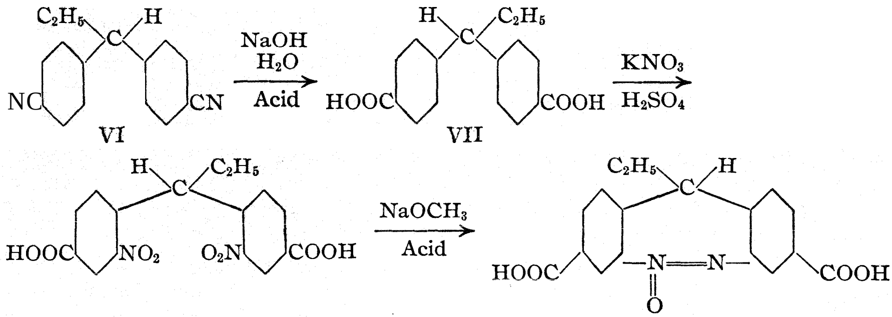
[2] Täuber, *Ber.*, **24**, 3083 (1891).

[3] Ullmann and Dieterle, *ibid.*, 37, 24 (1904).

[4] Duval, *Compt. rend.*, **141**, 198 (1905); *Bull. soc. chim.*, [4] 7, 527 (1910).

[5] King, *J. Chem. Soc.*, **117**, 988 (1920).

[6] Duval, Bull. *soc. chim.*, [4] 7,681 (1910).



VI VII VIII IX

In this series of reactions the first two steps have been previously described. The structure of ethyl-*bis*-(4-nitrophenyl)-methane (IV) was established by the fact that upon oxidation only p-nitrobenzoic acid could be isolated. The free diamino compound (V) was not isolated but was used in the form of its salt. The dicyano compound (VI) was never isolated in a pure state. The crude product was hydrolyzed directly to the dibasic acid (VII). The final product (IX) was quite insoluble and very high melting. This might be considered as an indication that the molecule was not a simple one but made up of a number of units connected through the nitrogen atoms. However, this did not seem likely as the solubility and melting point of the new compound resembled those of the azoxy compounds from m- and p-nitrobenzoic acids.[7]

An attempt was made to shorten the synthesis of the desired type of compound by nitrating the diamino compound (V) in sulfuric acid to give ethyl-bis-(2-nitro-4-aminophenyl)-methane and then to reduce this product to an azoxy compound. The nitro compound was obtained but the azoxy compound was not isolated in a pure form.

The cyclic azoxy compound (IX) became deeply colored in alkali and it was not possible to titrate it with alkali using indicators. It formed a dibrucine salt which was crystalline but deeply colored. This salt did not seem to separate into isomers on crystallization from alcohol. The attempted resolution was not conclusive as only one salt and only two solvents were used. The solutions were deeply colored and small rotations might have been overlooked. Further work is in progress on the resolution of this type of molecule.

Experimental Part

1,1-Diphenylpropene-1 was prepared according to the method of Sabatier and Murat[8] with the exception that ethylmagnesium bromide was substituted for the iodide. The yield on a three mole run was 68–70% of the theoretical amount. This hydrocarbon has previously been reduced by hydrogen in the presence of nickels and of plati-

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[7] Elliott, *J. Chem. Soc.*, *73*, 145 (1898).

[8] Sabatier and Murat, *Ann. chim.*, 4, 287 (1915).

num[9] but neither method was satisfactory for use on the amounts needed in this work. Klages[10] has mentioned its reduction by means of sodium and alcohol but has not given the details of the method.

Ethyl-bis-(phenyl)-methane (Formula III).—In a five-liter, two-necked flask fitted with an efficient reflux condenser and a mechanical stirrer was placed a solution of 300 g. of 1,1-diphenylpropene-1 in 1500 cc. of absolute alcohol. The stirrer was started and 150 g. of sodium, cut into small pieces, was introduced as rapidly as possible without loss of material through the condenser. This addition usually required about forty minutes. The flask was then heated until the sodium had entirely reacted. When necessary more alcohol was added. After the sodium was entirely in solution one liter of water was added and the alcohol was removed by steam distillation. The oily layer of hydrocarbon was separated from the water solution and the water extracted twice with a little ether. The ether extracts were added to the main body of the hydrocarbon, which was then dried over anhydrous sodium sulfate. The product was then distilled and the portion boiling at 129–131° (7 mm.) was collected and washed seven to ten times with cold concd. sulfuric acid to remove any diphenylpropene. When the sulfuric acid was no longer colored after shaking with the hydrocarbon, the latter was washed with water and again distilled. The yield of pure product boiling at 129–131° (7 mm.) was 260–275 g. (85–90% of the theoretical amount).

Ethyl-*bis*-(4-nitrophenyl)-methane (Formula IV).—In a three-liter, three-necked flask fitted with a mechanical stirrer were placed 314 *g.* of ethyldiphenylmethane and 340 cc. of concd. sulfuric acid (sp. gr. 1.84). The stirrer was started and the flask was surrounded by an ice-bath. When the temperature of the mixture reached about 10° a mixture of 230 cc. of concd. nitric acid (sp. gr. 1.42) and 570 cc. of concd. sulfuric acid was added with stirring over a period of one and one-half hours. The temperature was never allowed to go above 20°. Toward the end of the nitration a white gummy material began to precipitate out of solution.

Stirring was continued for about fifteen minutes after the addition of the last of the acid and then the reaction mixture was poured into four volumes of ice water. A gummy precipitate slowly settled on the bottom of the vessel. After this had separated, the aqueous acid layer was decanted and the residue was washed with water and then with ether. The ether dissolved some tarry material and left a white powder. This was recrystallized twice from acetic acid. In this way glistening white needles which melted at 143–144.5° were obtained. The yield was 180–190 g. (40–42% of the theoretical amount).

Anal. Subs., 0.2131: CO_2, 0.4190; H_2O, 0.0936. Calcd. for $C_{15}H_{14}O_4N_2$: C, 63.9; H, 4.9. Found: C, 63.2; H, 4.9.

A sample of the nitro compound was oxidized with chromic oxide in glacial acetic acid. The only oxidation product which could be isolated was p-nitrobenzoic acid, m. p. 238°.

Ethyl-*bis*-(4-aminophenyl)-methane Hydrochloride (Formula V).—A suspension of 15 g. of the nitro compound in 150 cc. of boiling alcohol was reduced with hydrogen in the presence of the platinum catalyst of Adams and Shriner.[11] The theoretical amount of hydrogen was absorbed in eleven minutes in the shortest run and in one hour in the longest. When the reduction was complete the catalyst was removed by filtration. An excess of concd. hydrochloric acid was added to the solution and it was then evaporated to dryness. The hydrochloride thus obtained weighed 15 *g.* (practically 100% of the theoretical amount). The salt was ground to a fine white powder. It melted at 232–235°.

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[9] Kern, Shriner and Adams, THIS JOURNAL, **47,** 1147 (1925).

[10] Klages, Ber., 35, 2648 (1902).

[11] Adams and Shriner, THIS JOURNAL, **45,** 2171 (1923).

Anal. Subs., 0.2165: 14.48 cc. of 0.1001 *N* $AgNO_3$. Calcd. for $C_{15}H_{20}N_2Cl_2$: Cl, 23.70. Found: Cl, 23.72.

The free amine was prepared by treating an aqueous solution of the hydrochloride with sodium hydroxide solution. The white crystalline product which separated darkened very rapidly in the air.

Ethyl-*bis*-(2-nitro-4-aminophenyl)-methane.—In a flask fitted with a mechanical stirrer and a separatory funnel was placed 400 cc. of concd. sulfuric acid. The stirrer was started and 30 g. of the diamine dihydrochloride was added in portions. Stirring was continued until the hydrogen chloride was expelled. The remaining solution was dark red in color. This solution was cooled to about 0° and a solution of 13 g. of concd. nitric acid in 22 cc. of concd. sulfuric acid was added from the separatory funnel at such a rate that the temperature did not go above 5".

After the nitrating mixture was added the solution was stirred for one-half hour while the temperature was maintained at 5°. The mixture, which had become opaque and more viscous, was then poured on a kilo of cracked ice. On standing some dark flocculent material separated This was removed by filtration. To the filtrate were added small portions of sodium carbonate. The first precipitate was tarry. This was removed by filtering and further addition of sodium carbonate precipitated the dinitro diamino compound as a yellow product. This material when collected on a filter and partially dried became resinous. The moist product was ground up with one and one-half times the theoretical amount of concd. hydrochloric acid and enough boiling water was added to dissolve the salt. This boiling solution was twice treated with decolorizing carbon (Norit) and filtered hot. The filtrate was then concentrated on a steam cone until crystals began to appear. On cooling the hydrochloride separated as grayish white crystals. These were collected on a filter and the filtrate was concentrated to give a second and third crop of crystals. After that tarry material began to separate and the mother liquors were discarded.

The hydrochloride obtained in the three crops of crystals was ground up with a slight excess of aqueous ammonia. The free dinitro diamine separated as an orange colored precipitate. It was collected on a filter, dried and recrystallized from boiling absolute alcohol. The product thus obtained melted at 146.5–148° after drying at 110°.

Anal. Subs., 0.2323: CO_2, 0.4793; H_2O, 0.1014. Calcd. for $C_{15}H_{16}O_4N_4$: C, 56.96; H, 5.12. Found: C, 56.52; H, 4.90.

An attempt was made to reduce this compound in the same manner that King6 had reduced 2,2′-dinitro-4,4′-diaminodiphenylmethane. Only tarry material was obtained. No other conditions for the reduction were investigated.

Ethyl-bis-(4-cyanopheny1)-methane (Formula VI).—The replacement of the amino groups by cyano groups in ethyl-*bis*-(4-aminophenyl)-methane was accomplished by the procedure described by Clarke and Read[12] for *p*-toluonitrile. The sodium cuprous cyanide solution was prepared by reducing a solution of 32 g. of copper sulfate and 8 g. of sodium chloride with 4.4 g. of sodium hydroxide and 6.6 g. of sodium bisulfite and dissolving the cuprous chloride thus obtained in a solution of 16 g. of sodium cyanide in about 200 cc. of water.

To a suspension of 15 g. of ethyl-bis-(4-aminopheny1)-methane hydrochloride in 50 cc. of water enough hydrochloric acid was added to give a solution distinctly acid to litmus paper. This mixture was cooled to 0° and 7 g. of sodium nitrite was added with stirring over a period of about ten minutes. The mixture was maintained at 0 to 5° for about another fifteen minutes or until a clear dark red solution resulted. The excess

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[12] Clarke and Read, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. IV, p. 69.

hydrochloric acid was neutralized by adding sodium carbonate. This neutral solution was added to the cold solution of sodium cuprous cyanide described above over a period of thirty minutes. Vigorous stirring was maintained during the addition and small portions of ether were added from time to time to break up the foaming. The reaction mixture was maintained at 0 to 5° for two hours after the two solutions were mixed and the temperature was then allowed to rise to 25° over a period of about two hours. Vigorous stirring was maintained during all of this time. The mixture was then slowly warmed to 50–60° with occasional stirring and filtered. The precipitate when dry was a light brown powder. It could not be recrystallized from any common solvents and it decomposed when an attempt was made to distil it under reduced pressure. This crude product was used directly in the preparation of the following acid.

Ethyl-bis-(phenyl-4-carboxylic acid)-methane (Formula **VII**).—The crude dicyano compound from two preparations of the size just described was added to 320 cc. of 20% aqueous sodium hydroxide solution and the mixture was boiled vigorously under a reflux condenser for about forty hours until no more ammonia was evolved. During the heating the powder gradually dissolved in the alkaline solution.

When the hydrolysis was completed the solution was cooled and acidified with excess hydrochloric acid. The crude dibasic acid separated as a brownish mass and was collected on a suction filter and washed with water. It was then dissolved in aqueous ammonia solution, and the solution was filtered and evaporated to dryness on a steam cone. The brownish salt was finely ground and extracted with two 200-cc. portions of warm (50°) water. From this solution the acid was thrown down as a voluminous white precipitate by the addition of excess hydrochloric acid. This precipitate retained considerable water. It was dried at 120° from four to six hours and then recrystallized from boiling glacial acetic acid using a little decolorizing carbon. After three recrystallizations from glacial acetic acid a white crystalline product was obtained. This was then dried for an hour at 120°. The yield was 6.2–6.6 g. (20–22% of the theoretical amount based on the diamine dihydrochloride) of a product which melted at 258–260°.

Neutral equivalent. Subs., 0.3000: 21.45 cc. of 0.0976 *N* NaOH. Calcd. for $C_{15}H_{14}(CO_2H)_2$: N. E., 142.1. Found: N. E., 143.1.

Anal. Subs., 0.2046: CO_2, 0.5394; H_2O, 0.1049. Calcd. for $C_{17}H_{16}O_4$: C, 71.9; H, 5.68. Found: C, 71.8; H, 5.46.

Ethyl-bis-(2-nitrophenyl-4-carboxylic acid)-methane (Formula **VIII**).—To a solution of 15.6 g. of the pure dibasic acid in 100 cc. of concd. sulfuric acid was added in portions 12 g. of powdered potassium nitrate. The temperature was held at 24–28° and vigorous stirring was maintained. After the reaction mixture showed no further tendency to evolve heat, it was allowed to stand for about twenty hours. Usually a white precipitate appeared on the top of the reaction mixture during this time. The material was poured into cold water and the dinitro dibasic acid separated as a yellowish gummy mass. It was filtered and recrystallized two or three times from boiling glacial acetic acid. The yield was 12.3 to 13 g. (60–65% of the theoretical amount) of a product which melted at 273–275°.

Anal. Subs., 0.2052: CO_2, 0.4140; H_2O, 0.0698. Calcd. for $C_{17}H_{14}O_8N_2$: C, 54.54; H, 3.77. Found: C, 55.00; H, 3.80.

The compound became deeply colored in alkaline solution and a satisfactory titration was not obtained.

Ethyl-2,2′-azoxydiphenylmethane-4,4′-dicarboxylic Acid (Formula **IX**).—To a solution of 1.3 g. of metallic sodium in 15 cc. of absolute methyl alcohol was added 2 g. of the above dinitro dibasic acid. The mixture was boiled under a reflux condenser for about five hours. After heating for a short time the sodium salt separated as a hard mass which was thee broken up with a stirring rod. A deep red color soon developed. After this heating period most of the alcohol was evaporated. The residue was dissolved in water and the solution cooled nearly to 0°. On the addition of excess hydrochloric acid the azoxy compound separated as a reddish-yellow solid. This was collected on a filter and washed thoroughly with dilute hydrochloric acid and then with dilute alcohol (80 cc. of 95% alcohol and 20 cc. of water). This treatment removed considerable color from the product. After drying the residue at 120°, it weighed 0.65 g. (36% of the theoretical amount). The product did not melt sharply. It slowly darkened above 270" and appeared to char completely at 320–330°. The product was an orange-colored powder. No success was met in any attempts at recrystallization. The compound was quite insoluble in all common solvents except pyridine and it showed little difference in solubility with change in temperature in this solvent. However, several preparations were tried and each gave the same product. Moreover, the following analyses on products made at different times indicated that the product thus obtained was quite pure.

Anal. Subs., 0.1993, 0.2267, 0.2130: CO_2, 0.4601, 0.5234, 0.4917; H_2O, 0.0768, 0.0881, 0.0837. Calcd. for $C_{17}H_{14}O_5N_2$: C, 62.55; H, 4.33. Found: C, 62.97, 62.96, 62.9; H, 4.30, 4.35, 4.39.

The Brucine Salt of 2,2′-Ethyl-azoxydiphenylmethane-4,4′-dicarboxylic Acid.—Ten grams of *l*-brucine was dissolved in 200 cc. of absolute alcohol and 4 g. of the azoxy acid was added. The solution was boiled under reflux condenser for about four hours and then filtered to remove a light red, insoluble precipitate. On standing 9.4 g. of a yellow crystalline compound separated from the filtrate. It was filtered and dried. It melted at 230–243° with considerable decomposition.

Anal. Sub., 0.1885: CO_2, 0.4717; H_2O, 0.1030. Calcd. for $C_{63}H_{66}O_{13}N_6$: C, 67.85; H, 5.96. Found: C, 68.2; H, 6.1.

A solution containing 0.0339 g. of salt per cc. of pyridine in a 1-dm. tube gave a rotation of $-1.6°$, $[\alpha]_D^{20}$ $-47.3"$.

The filtrate from this fraction was concentrated to about 100 cc. and another 2 g. of salt separated. This product had properties very similar to the insoluble material which first separated. A solution containing 0.0356 g. of salt per cc. of pyridine in a 1-dm. tube gave a rotation of $-1.56°$, $[\alpha]_D^{20}$ $-43.8°$.

The two fractions were treated with hydrochloric acid and the two samples of the free azoxy acid were dissolved in pyridine to give solutions containing about 0.02 g. of acid per cc. No rotation was observed in a 1-dm. tube.

Considerable difficulty was met in attempting to read the rotations on the salt and the acid as the solutions were deeply colored. A Schmidt and Haensch saccharimeter with a conversion factor of 0.3468 was used for taking the readings. The source of light was a 1000-watt projection lamp. The light was passed through a 3-cm. length of 3% potassium dichromate solution to screen out the blue and violet rays.

The brucine salt could be crystallized from water and came out in a better crystalline form containing water of hydration. A sample weighing 0.3448 g. was dried at 145–155° for four and one-half hours. The loss in weight was 0.0167 g. Calcd. for $C_{63}H_{66}O_{13}N_6 \cdot 3H_2O$: H_2O, 4.62. Found: H_2O, 4.84.

The insoluble fraction from water was less than from alcohol but again the free acid obtained from the salt showed no rotation.

Summary

1. A new cyclic azoxy compound has been prepared from a substituted diphenylmethane derivative.

2. An attempt to resolve this compound was not successful.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE REDUCTION OF BENZOPHENONE TO BENZOPINACOL BY MEANS OF MAGNESIUM AMALGAM AND SOME OBSERVATIONS CONCERNING MAGNESIOUS CHLORIDE

BY HENRY GILMAN AND ROBERT E. BROWN

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Introduction

In a recent paper by Gilman and Fothergill[1] it was shown that triphenylmethylmagnesium chloride probably dissociates in the following manner

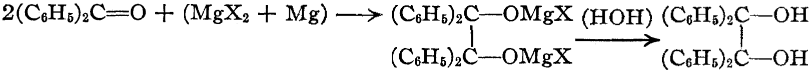
$$(C_6H_5)_3CMgCl \rightleftharpoons (C_6H_5)_3C— + —MgCl \qquad (I)$$

Evidence for such dissociation was the molecular weight determination, reduction of benzophenone to benzopinacol, catalytic reduction and the reaction with nitrous oxide.[2]

Attention was directed at that time to a serious objection that might be raised against a dissociation leading to the formation of the hypothetical magnesious chloride (—MgCl). If Reaction I were correct, then it is possible that the reaction might proceed irreversibly to give triphenylmethyl (or hexaphenylethane) and magnesium and magnesium chloride ($MgCl_2$). Such a possibility is reasonable on the basis of the following equilibrium.

$$2MgCl \rightleftharpoons Mg + MgCl_2 \qquad (II)$$

Gomberg and co-workers,[3] in some excellent studies, have shown that Reaction II, with magnesium iodide and magnesium bromide, is very largely displaced toward the right so that the quantity of magnesious halide (—MgX) present in solution is extremely small. They also established the fact that the binary system ($MgCl_2$ + Mg) quite unlike the binary systems ($MgBr_2$ + Mg) and (MgI_2 + Mg) does not reduce benzophenone, in the following manner, to benzopinacol.



$$2(C_6H_5)_2C{=}O + (MgX_2 + Mg) \longrightarrow \begin{array}{l}(C_6H_5)_2C—OMgX \\ \quad\ | \\ (C_6H_5)_2C—OMgX\end{array} \xrightarrow{(HOH)} \begin{array}{l}(C_6H_5)_2C—OH \\ \quad\ | \\ (C_6H_5)_2C—OH\end{array} \qquad (III)$$

But, because Gilman and Fothergill[1] actually obtained benzopinacol from benzophenone and triphenylmethylmagnesium chloride (apparently free of any magnesium), it seemed altogether reasonable that magnesious chloride, formed in accordance with Reaction I, reduced benzophenone to benzopinacol (Reaction III) like magnesious bromide or ($MgBr_2$ + Mg) and magnesious iodide or (MgI_2 + Mg).

The reduction (Reaction III) goes rapidly with (MgI_2 + Mg), less quickly with ($MgBr_2$ + Mg) and not at all with ($MgCl_2$ + Mg). Gom-

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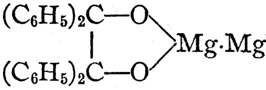
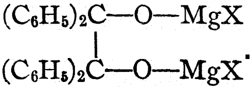
[1] Gilman and Fothergill, THIS JOURNAL, 51, 3149 (1929).

[2] Gilman and Leermakers, *ibid.*, 52, (1930).

[3] (a) Gomberg and Bachmann, *ibid.*, 49, 236 (1927); (b) Gomberg and Bachmann, *ibid.*, 49, 2666 (1927); (c) Gomberg and Bachmann, *ibid.*, 49, 2584 (1927); (d) Gomberg and Bailar, Jr., *ibid.*, 51, 2229 (1929); Gomberg and Van Natta, *ibid.*, 51, 2238 (1929).

berg and Bachmann[3a] attributed the absence of reduction with ($MgCl_2$ + Mg) to the sparing solubility of magnesium chloride in the ether–benzene mixture used as a medium. However, because magnesium chloride is soluble, even though to an extremely slight extent, in an ether–benzene mixture, it occurred to us that the system ($MgCl_2$ + Mg) should reduce benzophenone if the reaction were heated for an extended time. Previously, Gilman and Fothergill[1] confirmed the results of Gomberg and Bachmann[3a] on the absence of reduction by ($MgCl_2$ + Mg). The results of the present study complete such verification because benzophenone when heated in a sealed tube for 35 days at 130° with ($MgCl_2$ + Mg) gave neither the characteristic color indicative of reduction[3] nor any benzopinacol.

Other experiments were carried out to see if evidence might not be secured for the —MgCl postulated in Reaction I. It was found that benzophenone is reduced to benzopinacol by magnesium and mercuric chloride. We are of the opinion that such reduction is due to magnesium amalgam and not to the system ($MgCl_2$ + Mg), because as just stated ($MgCl_2$ + Mg) without mercury did not effect reduction, and also because magnesium and mercury (very probably as magnesium amalgam) did reduce benzophenone to the pinacol.[4] In their first study Gomberg and Bachmann[3a] reported that magnesium amalgam did not reduce the ketone, but later[3'] they reported that such reduction did occur but in an erratic fashion. We also tried magnesium cleaned with iodine and with a Grignard reagent (methylmagnesium iodide), but observed no reduction.

The results, on the whole, are not too easy of correct interpretation. It is clear that although magnesium alone will not effect reduction, magnesium in an activated form (as the amalgam by mercury or by mercuric halide) will reduce the carbonyl group. Quite naturally this raises a question whether reduction by the system (MgI_2 + Mg) or ($MgBr_2$ + Mg) might not be due to an activation of the metal by the magnesium halide, somewhat after the manner of its activation by the mercuric halide. If this were the case, an answer must be found to the need of an equivalent quantity of magnesium halide (or halogen). Possibly as in some other catalytic reactions (like some Friedel–Crafts reactions) the catalyst is required at moderate temperatures in equivalent molecular quantities because it is "accidentally removed" or tied up by the formation of complexes with intermediate compounds, the formation of which it accelerates. In such an event the formula of the intermediate halogen magnesium pinacolate might be  $\begin{matrix}(C_6H_5)_2C—O \\ | \\ (C_6H_5)_2C—O\end{matrix}\!\!>Mg{\cdot}MgX_2$ and not  $\begin{matrix}(C_6H_5)_2C—O—MgX \\ | \\ (C_6H_5)_2C—O—MgX\end{matrix}$. Gomberg and co-workers[3] have already considered

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[4] See also Schlenk and Thal, *Ber.*, 46, 2847 (1913).

the former compound as derivable from the latter by the application of heat.

It may not be an easy matter to answer the question whether the reduction is due to magnesious halide (—MgX) from the system (MgX_2 + Mg), or to the catalyzing or activating effect of the magnesium halide (MgX_2) on the magnesium. Possibly they are one and the same thing, or both processes are involved in concurrent reactions.[5]

TABLE I

RESULTS OF EXPERIMENTS

Run no.	Mg G.	Mg Atom	$(C_6H_5)_2CO$ G.	$(C_6H_5)_2CO$ Moles	$HgCl_2$, G.	Pinacol G.	%	Time of heating, Days	Temp., °C.
1	2.4	0.1	18.2	0.1	0.5	1.2	6.7	8	130
2[a]	1.2	.05	9.1	.05	None	None		35	130
3	1.2	.05	9.1	.05	None	None		8	130
4	1.2	.05	9.1	.05	0.5	None		8	130
5	0.0	.0	9.1	.05	None	None		8	130
6[b]	1.2	.05	9.1	.05	0.5	0.7	7.7	6	25
7[c]	1.2	.05	9.1	.05	None	0.3	3.3	35	130
8[d]	1.2	.05	9.1	.05	None	None		12	130
9[e]	1.2	.05	9.1	.05	None	None		1	25

[a] In this experiment 4.8 g. (0.05 mole) of magnesium chloride was used. Another experiment like this was run for eight days at 130° and no benzopinacol was obtained.

[b] In this experiment the reaction tube was shaken mechanically at room temperature.

[c] Ten g. of mercury was used in this experiment. No color appeared in the reaction mixture until it had been heated for fourteen days. When this run was worked up a yellow oil was isolated. It would not crystallize at low temperatures nor could it be made to yield a crystalline product from alcohol, ether, benzene, acetic acid, ligroin or methyl alcohol.

[d] The magnesium was first cleaned in this experiment by treating it with iodine. Of course, the iodine and magnesium iodide were then completely removed by an ether–benzene mixture washing in an inert atmosphere.

The magnesium which was cleaned by permitting it to react with methyl iodide in ether gave no color and no benzopinacol when heated with benzophenone for twenty-four hours at 130° in an ether–benzene mixture.

[e] In this experiment, 3.1 g. (0.05 mole) of magnesium fluoride was used. Our interest here was with other studies concerned with the preparation of phenylmagnesium fluoride from magnesium diphenyl. The reaction tube in this experiment was shaken mechanically at room temperature.

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[5] If a definite answer can be given, we feel quite certain that it will come from Gomberg and co-workers. This field is properly reserved to its discoverers who have done much with it and in a short time. Our interests lie only with such applications of their developments as concern the Grignard reagents. We (H. G.) are at present sympathetically inclined to the attractive magnesious halide conception [see Gilman and Fothergill, THIS JOURNAL, 50, 3334 (1928); and Gilman and Kirby, *ibid.*, 51, 1571 (1929)], but some of our students feel that a sufficiently strong case has not been made against that interpretation which involves an activated or catalyzed magnesium.

Experimental Part

All of the experiments were carried out in sealed tubes and with purified materials. Operations such as filtration were effected in an inert atmosphere.

Two and four-tenths g. (0.1 atom) of 30–80 mesh magnesium, 18.2 g. (0.1 mole) of benzophenone, 90 cc. of an ether–benzene mixture (in the ratio of 1:2), and the mercuric chloride or magnesium chloride, if used, were placed in a previously constricted, nitrogen filled Carius tube. The tube was evacuated, until the solvents boiled vigorously, and sealed off. It was then placed on a steam-plate, the temperature of which was 130°. At the end of the heating period, the tube was opened under a stream of nitrogen, the contents filtered through a nitrogen filled Erlenmeyer flask into the bottom of which was sealed a sintered glass filter, and the filtrate was allowed to run into a flask provided with a nitrogen atmosphere.

After adding dilute hydrochloric acid, the ether–benzene layer was separated, washed with water, dried over sodium sulfate and the solvents removed by distillation. One hundred cc. of dry petroleum ether (40–60°) was added and the insoluble pinacol was filtered, digested with 20 cc. of petroleum ether, filtered, dried and weighed.

Because benzopinacol decomposes near its melting point, parallel comparative melting points were always made with pure benzopinacol. The melting points varied from 183 to 189° depending on the rate of heating of the melting-point bath. Mixed melting-point determinations were always made with pure benzopinacol.

The separation of benzopinacol from benzophenone by means of 40–60° petroleum ether is very satisfactory when all of the benzene is removed from the mixture of pinacol and ketone. This was accomplished by blowing dry air over the warm mixture after the major portion of the solvents had been removed by distillation.

The results of a miscellany of experiments are given in Table I and the footnotes which accompany it.

Summary

In connection with the possible existence of magnesious chloride, a study has been made of some factors affecting the reduction of benzophenone to benzopinacol.

AMES, IOWA

[COMMUNICATION NO. 408 FROM THE KODAK RESEARCH LABORATORIES]

THE PREPARATION OF SYM.-DIPHENYLCARBAZIDE

BY C. R. NOLLER

RECEIVED OCTOBER 7, 1929 PUBLISHED MARCH 6, 1930

Sym.-diphenylcarbazide has come into considerable use for the detection of various metallic radicals, particularly chromium.[1] On attempting to prepare this compound by heating urea with an excess of phenylhydrazine, it was found difficult to obtain products from different runs having uniform melting points. Moreover, the melting points given in the literature vary between 151 and 171°.[2]

The melting point of 163–164° has been given frequently and a product melting sharply at this point (uncorrected) was often obtained in our work. It was found that this substance is an addition compound of one mole of *sym.*-diphenylcarbazide with one mole of 1-phenylsemicarbazide. This was shown by analysis, by determining the melting points of mixtures of known percentages of pure *sym.*-diphenylcarbazide and 1-phenyl semicarbazide, and also by the fact that the melting point of the double compound is lowered when mixed with either pure diphenylcarbazide or pure phenylsemicarbazide, but not when mixed with an intimate mixture of equimolar portions of these two compounds. Because of the slow de-

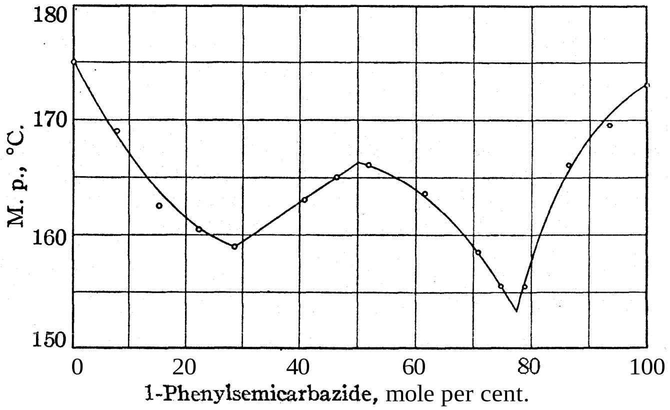

Fig. 1.—Melting-point curve of mixtures of *sym.*-diphenylcarbazide with 1-phenylsemicarbazide.

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[1] Stover, THIS JOURNAL, 50, 2363 (1928).

[2] (a) Skinner and Ruheman, Ber., 20, 3372 (1887), m. p. 161° (see ref. 2 h.); (b) Fischer, *ibid.*, 22, 1935 (1889), m. p. 163–164°; (c) Heller, Ann., 263, 272 (1891), m. p. 163°; (d) Cazeneuve and Moreau, Bull. *soc.* chim., [3] 23, 53 (1900), m. p. 169–170°; (e) Oddo, *Atti.* accad. *Lincei*, [5] 12, 435 (1903), m. p. 168–169°; (f) Metzger and Zons, J. Ind. Eng. *Chem.*, 4, 493 (1912), m. p. 150–151°; (g) Barnebey and Wilson, THIS JOURNAL, 35, 157 (1913), m. p. 163.5°; (h) Bamberger, Padova and Ormerod, Ann., 446, 285 (1925), m. p. 171°.

composition of all the materials at the melting point it was not possible to determine cooling curves accurately and all melting points were determined by the capillary tube method. For the same reason the mixed melting points had to be determined on material that was intimately ground together rather than on fused material. Because of the wide range of the melting points of the mixtures, the figures given in the table are the temperatures at which the material first definitely wet the side of the capillary tube. This point could be checked readily on separately prepared mixtures within 1°. The experimental results are given in the accompanying tables and graph and show a possible explanation of the discrepancy in the melting points recorded in the literature where 1-phenylsemicarbazide is a possible product. Cazeneuve and Moreau[2d] note that an alteration in the appearance of *sym.*-diphenylcarbazide takes place at 151° but that this is not the melting point. We have noted at times a similar change at about 158° (corr.) but the true melting point of the pure material is quite sharp.

ANALYSES

	M. p. (corr.), °C.	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found
Sym.-diphenylcarbazide ($C_{13}H_{14}N_4O$)	175–175.5	64.46	64.00	5.79	5.88
			64.09		5.88
1-Phenylsemicarbazide ($C_7H_9N_3O$)	173–173.5	55.63	55.87	5.96	6.11
			55.69		6.04
Double compound of *sym.*-diphenylcarbazide and 1-phenylsemicarbazide ($C_{20}H_{23}N_7O_2$)	166–166.5	60.05	60.22	5.88	5.86
			60.44		5.94

MELTING POINTS OF MIXTURES OF *sym.*-DIPHENYLCARBAZIDE AND 1-PHENYLSEMICARBAZIDE

1-Phenylsemicarbazide Weight, %	1-Phenylsemicarbazide Mole, %	M. p., (corr.), °C.	1-Phenylsemicarbazide Weight, %	1-Phenylsemicarbazide Mole, %	M. p., (corr.), °C.
0	0	175	50	61.5	163.5
5	7.8	169	60	70.6	158.5
10	15.1	162.5	65	74.8	156
15	22.1	160.5	70	78.9	156
20	28.5	159	80	86.4	166
30	40.8	163	90	93.5	169.5
35	46.2	165	100	100.0	173
40	51.6	166			

In order to purify the *sym.*-diphenylcarbazide prepared from urea and phenylhydrazine, it is necessary to extract the crude product with boiling distilled water repeatedly and with vigorous stirring until the melting point no longer changes. Although 1-phenylsemicarbazide is quite soluble in hot water, it is only slowly extracted from the double compound. During this process a red color develops, even when the water used for extraction has been boiled previously to remove dissolved air. This color is readily removed by washing with small portions of cold acetone, followed by a final crystallization from acetone. The product thus obtained contains one mole of acetone of crystallization, which is best removed by adding cold benzene to the dried product, heating to boiling, allowing to cool and filtering. Neither 1-phenylsemicarbazide nor the double compound forms an addition product with acetone.

By using the method of Cazeneuve and Moreau,[2d] who reacted phenylhydrazine with diphenyl carbonate or guaiacol carbonate instead of urea, no 1-phenylsemicarbazide is formed and the necessity for this troublesome purification is eliminated. Because it is available commercially, guaiacol carbonate is more suitable than diphenyl carbonate, although the latter gives slightly better yields. The original procedure of Cazeneuve and Moreau has been modified so that the *sym.*-diphenylcarbazide is more readily isolated in a pure state, and so that the guaiacol formed in the reaction and the excess phenylhydrazine are recovered in good yields. The same procedure has been used with equal success in runs using as much as 8 moles of guaiacol carbonate.

Preparation of *Sym.*-**Diphenylcarbazide.**—A mixture of 54.8 g. (0.2 mole) of guaiacol carbonate and 86.4 g. (0.8 mole) of phenylhydrazine is heated in an oil-bath at 160–165° (thermometer in liquid) for two hours with occasional shaking. The mixture is poured out into an open dish and after it has cooled it is stirred until crystallization begins. It is allowed to stand for several hours at 15° to allow complete crystallization and is then worked to a paste and extracted repeatedly with benzene until entirely free of phenylhydrazine and guaiacol. The pure white product melts at 175–175.5° (corr.) and the yield is 34-35 g., or 70–72% of the calculated amount.

Recovery of Phenylhydrazine and **Guaiacol.**—The benzene extracts obtained above are combined and dry hydrogen chloride passed in until the mixture becomes too pasty for good mixing. The phenylhydrazine hydrochloride is filtered with suction and thoroughly washed with benzene. The combined filtrates are treated again with hydrogen chloride and the process is repeated until the precipitate becomes distinctly pink. Hydrogen chloride is then passed in until nothing further precipitates, and the red and sometimes sticky solid that is formed is filtered and discarded. The combined crops of phenylhydrazine hydrochloride are practically white and weigh 53 g. (0.37 mole), which is almost the calculated amount recoverable. The pure free base was obtained from the hydrochloride in 80% yields.

The benzene solution, after the removal of all material that can be precipitated with hydrogen chloride, is distilled from a steam-bath at reduced pressure to remove the benzene, and the residue distilled in *vacuo*. There is obtained in this way 19 g. of guaiacol (70% of the calculated amount), boiling at 103–105" at 22 mm., m. p. 26–28".

Summary

1. It has been found that compound formation takes place between *sym.*-diphenylcarbazide and 1-phenylsemicarbazide, and this is offered as a possible explanation of the discrepancy in the melting points of *sym.*-diphenylcarbazide recorded in the literature.

2. A satisfactory method for the preparation of pure *sym.*-diphenylcarbazide is given.

Rochester, New York

[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, COLLEGE OF MEDICINE, OHIO STATE UNIVERSITY]

THE OCCURRENCE OF ARACHIDONIC ACID IN LARD[1]

BY J. B. BROWN AND E. M. DECK

RECEIVED OCTOBER 11, 1929 PUBLISHED MARCH 6, 1930

The fats and oils of warm-blooded animals are composed mainly of the glycerides of palmitic, stearic and oleic ($C_{18}H_{34}O_2$) acids. The presence of acids of lower molecular weight than palmitic is by no means unusual. Moreover, in a number of instances acids more unsaturated than oleic have been found, particularly linolic acid, $C_{18}H_{32}O_2$. The occurrence of linolenic ($C_{18}H_{30}O_2$) and clupanodonic ($C_{18}H_{28}O_2$) acids with three and four double bonds, respectively, has been rarely described, except in instances where these acids have been furnished the animal with the food. The fat of marine mammals such as the polar bear has been shown to contain considerable quantities of the characteristic highly unsaturated fish oil fatty acids, this no doubt being mainly a dietary effect.

Recent investigations have shown the presence of considerable quantities of arachidonic acid, $C_{20}H_{32}O_2$, in the lipids of the liver,[2] brain,[3] kidney, lung, pancreas,[3c] thyroid, suprarenal, spleen[4] and corpus luteum.[5] The lipids of these tissues differ markedly from the body fat in that they are more unsaturated and contain notable amounts of phospholipids together with other compounds of complex composition.

The writer in **1917** isolated from a specimen of woodchuck fat hexabromostearic acid corresponding to 3.0% of linolenic acid. The bromide was identified on the basis of melting point.[6] In an analysis of a specimen of human fat Eckstein found **0.33%** of arachidonic acid.[7] Isbell and Ellis,[8] in studying the soft pork problem, found arachidonic acid in amounts varying from **0.02** to **0.21%** in lards from hogs which had been fed on a number of experimental diets. In connection with their work, it is interesting to note that the largest amount of the acid occurred in lard from peanut-fed animals. The acid may have been formed therefore by desaturation of the arachidic acid in the diet.

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[1] Presented at the fall meeting of the American Chemical Society, 1929, Minneapolis, Minnesota

[2] P. Hartley, J. *Physiol.*, 38, 353 (1909); P. A. Levene and H. S. Simms, J. *Biol. Chem.*, 48, 185 (1921); J. B. Brown, *ibid.*, 80,455 (1928).

[3] (a) P. A. Levene and I. P. Rolf, *ibid.*, 54, 91 (1922); 54, 99 (1922); (b) L. G. Wesson, *ibid.*, 60, 183 (1924); (c) W. R. Bloor, *ibid.*, 80, 443 (1928); (d) J. B. Brown, *ibid.*, 83, 783 (1929).

[4] J. B. Brown, *ibid.*, 83,777 (1929).

[5] G. F. Cartland and M. C. Hart, *ibid.*, 66, 619 (1925).

[6] Unpublished research with Dr. G. D. Beal, University of Illinois (1917).

[7] H. C. Eckstein, J. *Biol. Chem.*, *64*, 797 (1925).

[8] N. R. Ellis and H. S. Isbell, *ibid.*, 69,219,239 (1926).

Tha object of the present work was to find whether arachidonic acid occurs in commercial lard as it is marketed today. Four specimens of lard from different packing houses were converted into methyl esters and analyzed. Methyl octobromo-arachidate was isolated from each by bromination in cold ether. The yields corresponded to an arachidonic acid content of 0.31 to 0.40%. The bromide was identified on the basis of correct melting point and bromine content. One specimen of the methyl esters was distilled under reduced pressure into four fractions. The content of arachidonic acid increased with boiling point from 0.07 to 0.66%, which results are in agreement with the fact that it is the highest boiling of any of the acids present. The fatty acids of lard are stated by Lewkowitsch[9] to consist of lauric, myristic, palmitic, stearic, oleic and linolic acids (with possibly small amounts of linolenic acid).

Direct bromination of lard yielded small amounts of ether-insoluble material which contained from 7.13 to 10.56% of bromine. No definite evidence concerning the nature of this material was obtained. Assuming it to be a pure compound containing one molecule of octobromo-arachidic acid, it would have a total molecular weight of about 6000. However, there was evidence that the substance was a mixture of a brominated mixed glyceride of arachidonic acid with four parts of palmito-distearin.

The amount of arachidonic acid present in the four specimens examined was roughly proportional to the iodine number.

The results obtained on composite commercial samples of lard are in agreement with those of Ellis and Isbell on lard from hogs on special diets. The arachidonic acid content reported above is over three times that reported by the latter investigators, who found a variation from 0.02 to 0.21% with an average of 0.09%. This is largely due, however, to the method of calculation. Ellis and Isbell found the percentage of arachidonic acid by calculating the acid content of the ether-insoluble bromides. This result, as has been stated by the writer in a previous paper,[2] is probably far too low, since pure arachidonic acid gives a polybromide number of only 80, or a yield of ether-insoluble bromides about one-fourth the theoretical.

The finding of arachidonic acid in lard is contrary to the usual statement that warm-blooded animal fats do not contain acids more unsaturated than linolic.

Experimental Part

Lard.—Four specimens of lard were purchased in original containers on the market. Two of these were the best products of Chicago packers, one of a Columbus packer, and the fourth specimen was marketed under a trade name by a chain store in Columbus. These samples represent typical lard as prepared commercially in the United States today.

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[9] Lewkowitsch, "Technology of Oils, Pats and Waxes," 1922, 6th ed., Vol. II, p. 709.

Analytical Methods.—The usual methods of analysis for iodine and saponification numbers were employed.

The polybromide number, *i. e.*, the percentage yield of bromides, was found by brominating weighed samples in cold ether, allowing to stand several hours, removing the ether by centrifugation and washing four times more with fresh cold ether, stirring each time. The white product was dried for several hours in a warm oven (not over 50°). The polybromide numbers of the esters from lard were so small that it was necessary to brominate 500-g. samples in one liter of ether to get large enough specimens for the bromine determination. The product was transferred to a 250-cc. centrifuge bottle for the first washing, and to a 50-cc. tube for final washings and weighing.

Bromine analyses were made by the Parr peroxide bomb method as modified by Brown and Beal.[10]

Arachidonic acid was determined according to the following formula

$$\%\ \text{arachidonic acid} = \frac{\text{polybromide number of ester}}{77.6} \times 100$$

where 77.6 is the polybromide number of pure methyl arachidonate. This method of calculation has been discussed previously.[4]

Preparation of Methyl Esters.—One kilo of lard was transferred to a 5-liter pyrex flask and refluxed for eighteen hours with 1200 cc. of dry methyl alcohol containing 1 to 2% of hydrogen chloride gas. The esters and alcohol were poured into 2 liters of cold water. Separation was facilitated by the addition of a handful or two of salt. The ester layer was removed and transferred to a 2-liter Claisen flask. The esters were warmed under reduced pressure. After small amounts of water and methyl alcohol had passed over, the esters were distilled: yield, 968, 961, 923. and 976 g. of water-white esters from 1-kilo lots of the four lards, respectively. Analyses of the samples of lard and methyl esters are given in Table I.

TABLE I

ANALYSIS OF FOUR SPECIMENS OF LARD AND RESULTANT METHYL ESTERS

Lard no.	B. p., °C.	Iodine number	Saponification number	Polybromide number	Br, %	Arachidonic acid, %
			Lard			
1	.....	58.55	195.7	..	...	..
2	.....	64.55	197.4	1.5	10.56	..
3	.....	59.78	199.7	..	...	..
4	.....	65.33	197.9	3.0	7.13	..
			Methyl Esters			
1	170.210 (4 mm.)	56.39	195.4	0.24	66.70	0.31
2	170.220 (6 mm.)	62.34	193.5	.28	66.30	.35
3	165.220 (6 mm.)	58.53	192.7	.25	66.46	.32
4	170.220 (6 mm.)	63.56	194.4	.31	66.44	.40

The bromide from Lard 3 in Table I, containing 10.56% of bromine, was further studied. Most of it melted at 60–70°, forming a distinctly turbid melt. This turbidity disappeared at about 180°. The material was soluble in chloroform, but sparingly soluble in ether and n-butyl alcohol at ordinary temperature. It was freely soluble in boiling butyl alcohol and toluene, and was crystallized from the former, giving tufts of needles. The product of crystallization contained 12.73% of bromine. It is probable that the material was a mixture, therefore, of 4 to 5 parts of α-palmito-distearin,

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[10] J. B. Brown and G. D. Beal, THIS JOURNAL, 45,1289 (1923).

which melts at 68° and is sparingly soluble in ether, with one part of brominated mixed glyceride, containing one molecule of octobromo-arachidic acid. α-Octobromo-arachido-distearin should contain 41.3% of bromine. α-Palmito-distearin has been isolated from lard by Bömer.[11]

Fractionation of Methyl Esters.—Six hundred and twenty-five g. of the methyl esters from Lard 1 was distilled slowly from a 1-liter Claisen flask, four fractions being cut. The results of analysis of these fractions are given in Table II.

TABLE II

RESULTS OF FRACTIONATION OF METHYL ESTERS FROM LARD NO. 1

B. p., °C.	Wt., g.	Iodine number	Sapon. number	Polybromide number	Arachidonic acid, %
180–194	114	42.73	203.3	0.05	0.07
194–199	181	49.98	199.0	.07	.09
199–210	222	62.03	195.4	.13	.17
210–220	105	72.82	190.9	.51	.66

The identity of the methyl octobromo-arachidate isolated from the methyl esters from each specimen of lard is proved by the bromine analyses, which agree satisfactorily with the theoretical, 66.78%, and by the melting point, which in each case was 228–230°, the same as that found for this compound isolated from the glandular lipids.

Summary

Four specimens of typical commercial lard have been found to contain arachidonic acid in amounts varying from 0.31 to 0.40%. Two of the samples of lard yielded ether-insoluble bromine addition products which were shown to be a mixture, probably of a-palmito-distearin with a glyceride of octobromo-arachidic acid.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

ALLENE AND METHYLACETYLENE TETRABROMIDES[1]

BY CHARLES D. HURD,[2] R. N. MEINERT[3] AND L. U. SPENCE[3]

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Methylacetylene tetrabromide was studied by Oppenheim[4] in 1864, and by Gustavson and Demjanov[5] in 1888. The more recent and more

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[11] Bomer, *Z. Nahr. Genussm.*, 17,393 (1909); 25,354 (1913).

[1] This paper contains results obtained in an investigation on "The Non-Catalytic Thermal Decomposition of Pure Hydrocarbons and Related Compounds," listed as Project No. 18 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Company. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

[2] Director, Project No. 18.

[3] American Petroleum Institute Junior Research Fellow.

[4] Oppenheim, *Ann.*, 132, 124 (1864).

[5] Gustavson and Demjanov, *J. prakt. Chem.*, [2] 38,201 (1888).

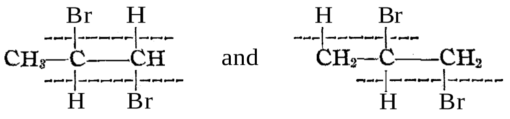
extensive data of both Risseghem[6] and of Demjanov and Dojarenka[7] seem to be more reliable, but in both cases the possibility of the presence of isomers seems not to have been eliminated. Risseghem prepared her material by the following steps: $CH_2{=}CBr{-}CH_3 \xrightarrow{Br_2} CH_2Br{-}CBr_2{-}CH_3 \xrightarrow{C_6H_5ONa} CHBr{=}CBr{-}CH_3 \xrightarrow{Br_2} CHBr_2CBr_2CH_3$. It will be noted that if sodium phenylate caused the detachment of hydrogen bromide in another direction, then $CH_2Br{-}CBr{=}CH_2$ would be formed, which, with bromine, would give allene tetrabromide, $CH_2Br{-}CBr_2{-}CH_2Br$. Demjanov and Dojarenka's tetrabromide is open to objection also. They decomposed trimethylcyclopropylammonium hydroxide at 300° to produce cyclopropene admixed with about 10% of allylene. Bromination yielded the tetrabromides $CHBr_2CH_2CHBr_2$ and $CH_3CBr_2CHBr_2$. Separation of these two compounds from each other, and possibly from traces of allene tetrabromide as well, by distillation methods makes it probable that the separation was not absolutely quantitative in spite of a rigorous procedure.

In the present work methylacetylene was prepared and passed into a solution of bromine in carbon tetrachloride. The methylacetylene tetrabromide thus produced was purified by fractional distillation. Three distinct methods were used in the synthesis of methylacetylene. In one method a satisfactory synthesis of propionaldehyde was effected, and this aldehyde was converted into propylidene chloride. The latter was then subjected to the action of potassium hydroxide in hot butyl alcohol

$$CH_3CH_2CHCl_2 + 2KOH \longrightarrow CH_3C{\equiv}CH + 2KCl + 2H_2O$$

Because of poor yields throughout, this method is not to be recommended. Reboul[8] carried out a similar reaction in a sealed tube at 150°, using ethyl alcohol.

Propylene bromide, in the second method, was converted into methylacetylene[9] by the action of potassium hydroxide in butyl alcohol. This methylacetylene was shown to be admixed with 4 to 7% of allene. Inspection of the formula of propylene bromide shows why this is possible



$$CH_3{-}\overset{Br}{\underset{H}{C}}{-}\overset{H}{\underset{Br}{C}}H \quad \text{and} \quad \overset{H}{CH_2}{-}\underset{H}{C}{-}\overset{Br}{\underset{Br}{CH_2}}$$

By liquefaction of the methylacetylene, and by two fractionations with a very efficient column the allene content was lowered from 5.5 to 1.2%.

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[6] Risseghem, Bull. *soc. chim. Belg.*, 28,376 (1919); *Chem. Zentr.*, I, 892 (1923).

[7] Demjanov and Dojarenka, *Ber.*, 56,2200 (1923).

[8] Reboul, *Compt. rend.*, 82, 377 (1876).

[9] Tapley and Giesy, *J. Am. Pharm. Assocn.*, **15**, 115 (1926).

The difficulty of complete purification by this means is obvious, since allene boils at −32° and methylacetylene at −27.5°.

It would seem that a mixture of methylacetylene and allene could be separated readily through metallic derivatives of the former, and further study may show this to be the case. Our preliminary experiences, however, with the cuprous salt and with the chloromagnesium derivative were so unsatisfactory that further efforts in this direction were abandoned. The cuprous salt was precipitated by passing the gas (83% methylacetylene, 10% allene, 7% air) into an ammoniacal solution of cuprous chloride. Decomposition of this cuprous methylacetylide with hydrochloric acid was unsatisfactory since it gave only a small yield of methylacetylene. In another attempt to purify a similar mixture of methylacetylene and allene, it was allowed to react with ethylmagnesium chloride in dry ether. This gave a precipitate of methylethynylmagnesium chloride, $CH_3C{\equiv}C{-}Mg{-}Cl$. Hydrolysis of this substance yielded a gas which was about 85% methylacetylene and the remainder hydrogen, ethane, etc. Since the recovery was only about 30% of the theoretical, no efforts were made to perfect the method.

In the third method, pure methylacetylene (entirely free from allene) was prepared by the action of sodium acetylide and methyl iodide in liquid ammonia. This is the method of Lebeau and Picon.[10] It has been used by Maass and Wright[11] for the synthesis of pure methylacetylene. As in the second method, this methylacetylene was purified by liquefaction and distillation. Admixed acetylene was thereby removed.

Boiling point, index of refraction and density determinations on these samples of methylacetylene tetrabromide were made and studied. Similar determinations were made on pure allene tetrabromide, $CH_2Br{-}CBr_2{-}CH_2Br$. This was prepared by the addition of bromine to allene, and by the addition of bromine to dibromo-2,3-propene-1, $CH_2{=}CBr{-}CH_2Br$. Work on allene tetrabromide has been reported by Gustavson and Demjanov[5] and by Lespieau.[12]

Experimental Part

Preparation of Propionaldehyde.—Propionaldehyde was prepared by the gradual addition of dichromate oxidizing mixture to hot n-propyl alcohol. Thus, for 100 g. of the alcohol, the oxidizing agent was composed of 164 g. of potassium dichromate, 120 cc. of concd. sulfuric acid and one liter of water. The alcohol was kept boiling during the addition, which took about thirty minutes. Efficient mechanical stirring was essential to facilitate the rapid escape of the aldehyde. A reflux condenser kept at 60° allowed this escape, but at the same time prevented the unoxidized propyl alcohol from distilling away. Propionaldehyde was then condensed and purified in the usual way The yield of aldehyde, b. p. 48–55°, was 44–47 g., or 45–49% of the theoretical.

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[10] Lebeau and Picon, *Compt.* rend., 156, 1077 (1913).

[11] Maass and Wright, THIS JOURNAL, 43, 1098 (1921).

[12] Lespieau, *Ann. chim. phys.*, [7] 11, 252 (1897).

Propylidene chloride was prepared in about 30% yields from propionaldehyde and phosphorus pentachloride by the method of Reboul.[13] It boiled at 86–88'.

Preparation of **Methylacetylene. First Method.**—Since preliminary dehalogenation experiments using a suspension of sodamide in paraffin oil gave very unsatisfactory yields of methylacetylene, this reagent was discarded in favor of potassium hydroxide in butyl alcohol.

One mole (56 g.) of potassium hydroxide was dissolved in 150 cc. of *n*-butyl alcohol in a 500-cc. flask fitted with a 5-bulb reflux condenser. The upper end of the condenser was fitted with a stopper which held a dropping funnel and a gas delivery tube. This tube was connected to two bromine wash bottles which contained a total of 30 cc. of bromine covered by water. Propylidene chloride (20 g.) was added dropwise through the funnel during twenty minutes. Heating was continued for an hour. Then the gas was swept out by a current of air for fifteen minutes.

The bromine layer was washed with saturated sodium sulfite solution, then with water. Five cc. of carbon tetrachloride was used to extract the emulsified portion. After drying and removal of the solvent, 1.8 g. was collected at 6 mm. below 93°, chiefly at 55–60°. This was undoubtedly CH_3—CHBr—CHClBr. The allylene tetrabromide fraction, 93–99", weighed 4.1 g., leaving 1.4 g. of residue. The allylene tetrabromide was fractionated and the constants taken on the portion boiling at 95–98° and 5.5–6 mm.

Preparation of Methylacetylene. Second **Method.**—Propylene[14] was converted into propylene bromide, which (202 g.), in turn, was dropped slowly into a flask containing a boiling solution of potassium hydroxide (180 g.) in n-butyl alcohol (400 cc.) as recommended by Tapley and Giesy. The methylacetylene and allene mixture thus produced escaped through an attached reflux condenser and was dried by passage through a calcium chloride tower. It was then liquefied by passing it into a small steel gas-bottle which was cooled to −55°; yield, 75%. For analysis, 100-cc. gaseous portions were treated with alkaline potassium iodomercurate solution for the acetylene content, and then with 82.5% sulfuric acid for the allene content.[15] In this way it was established that the gas contained about 5.5% (by volume) of allene and 94.5% of methylacetylene.

The liquefied hydrocarbon mixture was fractionally distilled from a spiral, vacuum-jacketed column such as has been described by Davis.[16] The distillate was collected in two portions of about equal volume, the first analyzing 9.2% of allene and the second 2.6%. Refractionation of the second fraction similarly yielded a higher-boiling portion which was found to contain 1.2% of allene. This material was converted into the tetrabromide, since it was not considered practical to fractionate it further.

For the bromination, the methylacetylene was allowed to escape slowly from its steel container and to pass into a solution of bromine in carbon tetrachloride. At the conclusion of the reaction, the excess of bromine was destroyed with an alkaline wash, and the tetrabromide dried and distilled in *vacuo.* The portion boiling from 95–110" (10 mm.) was collected. It weighed 23 g. This fraction, on redistillation, gave 13 g. of material boiling from 106–110° (10 mm.), which was used for the determination of its physical constants.

Preparation of Methylacetylene. Third Method.—Pure methylacetylene, free from allene, was made essentially by the method of Lebeau and Picon[10] from 36 g. of sodium metal (dissolved in liquid ammonia), an equivalent quantity of acetylene and

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[13] Reboul, Ann, *chim. phys.,* [5] 14,458 (1878).

[14] The propylene was generously furnished by E. R. Squibb and Sons. This courtesy is gratefully acknowledged.

[15] Hurd and Spence, THIS JOURNAL, 51, 3356 (1929).

[16] Davis, Ind. *Eng. Chem* , *Anal. Edition,* 1, 61 (1929); the column was constructed by Mr. George Reppert.

210 g. of methyl iodide. During the addition of methyl iodide, the temperature was maintained at −60 to −50°. When completed, the reaction flask was lifted from the cooling bath and the effluent gas was washed with water, with 10% sulfuric acid, then dried with calcium chloride, liquefied at −75° and finally fractionally distilled with the efficient column mentioned above to separate it from admixed acetylene. The last two-thirds of the distillate was used in preparing the tetrabromide, a step which was carried out in precisely the manner outlined in the second method. Fifty-eight g. of the tetrabromide, b. p. (10 mm.) 95–110°, was collected. On fractionation, 39 g. at 105–107° and 9 mm. was isolated.

Physical Constants of Methylacetylene Tetrabromide.—Our data will be compared and supplemented with the data of other workers. As stated above, our most reliable data were obtained on the material from the third method. That from the second contained small amounts of allene tetrabromide, whereas the quantity of material from the first was too small for rigorous purification.

PHYSICAL CONSTANTS OF METHYLACETYLENE TETRABROMIDE

The melting point, as noted by Risseghem, is −12.5"

Investigator		Boiling point °C.	Mm.	Density d	Temp., °C.	Index of refraction n_D	Temp., °C.
Oppenheim		225–230	760	2.94	0/0	....	...
Oppenheim		110–130	10	....	....	....	...
Risseghem		111	11	2.6661	17.4/4	1.6148	17.4
Demjanov and Dojarenka		122–123	19	2.6835[a]	0/0	1.6142	10
Demjanov and Dojarenka		.....	...	2.6652"	10/0	1.6169	20.5
Petersen[17]		119–121	17	....	....	....	...
Present investigation	First method	95–98	5.5/6	2.698	20/4	1.6217	11
		.....	...	....	....	1.6165	21
	Second method	106–110	10	2.693	20/4	1.6204	10.0
		.....	...	2.680	25/4	1.6159	18.7
		.....	...	....	....	1.6153	20.0
		.....	...	....	....	1.6131	24.4
		.....	...	....	....	1.6119	27.0
	Third method	105–107	9	2.699	15/4	1.6207	12.3
		.....	...	2.687	20/4	1.6186	16.6
		.....	...	2.676	25/4	1.6166	20.0
		.....	...	....	....	1.6140	25.4

[a] Also from different material, these values are given: 2.7225, 0°/4°; 2.7011, 10°/4°; 2.6800, 21°/4°.

Discussion of Data

The boiling point data have been plotted as a Dühring line[18] in Fig. 1. Thus the boiling point of methylacetylene tetrabromide and the boiling point of water at the same pressure are plotted on the same coordinate. Extrapolation of the curve to 100° for water (atm. press.) gives a value of 229° for the boiling point of methylacetylene tetrabromide. This is well in keeping with Oppenheim's observation. His value at 10 mm.,

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[17] Petersen, *Z. Elektrochem.*, 18, 712 (1912).

[18] Leslie and Carr, *Ind. Bng. Chem.*, 17, 810 (1925).

however, is distinctly off the curve. The remaining values fit the straight line curve fairly well.

The density values, referred to water at 4°, are plotted on Fig. 2, and the index of refraction data on Fig. 3. In Fig. 2 the results of Demjanov and Dojarenka are included. Our most reliable density values, those from the third method, were taken for this. This reliability was caused not only by the greater purity of the material but also by the fact that a 12-cc. specific gravity bottle was used as opposed to a 2.3-cc. Ostwald pycnometer which was employed for the other two methods. The other density values recorded in the literature vary considerably from these, all except Oppenheim's being smaller.

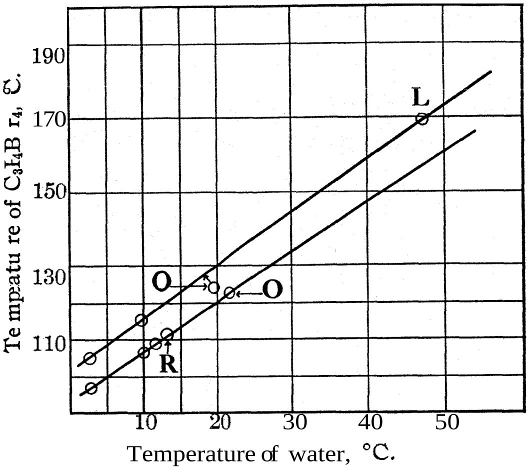

Fig. 1.—Dühring lines: O,O, data of Demjanov and Dojarenka; L, Lespieau's observation; R, Risseghem's datum; unmarked points from this investigation. Upper, allene tetrabromide–water; lower, methylacetylene tetrabromide–water.

The index of refraction values of Methods 1 and 3 are plotted in Fig. 3. The values for the material of Method 2 (from propylene bromide), if plotted, would show a parallel curve, the values throughout being somewhat smaller. Demjanov and Dojarenka's value at 21° (1.617) is of the correct order of magnitude but the value at 10° (1.6142) is evidently in error. This becomes obvious on plotting these two points. Risseghem's observation is somewhat low.

Allene Tetrabromide

Preparation from **Allene.** First Method.—A sample of dibromo-2,3-propene-1, prepared according to the method of "Organic Syntheses,"[19] and of b. p. 73–76" at 75 mm., was dehalogenated into allene. To do this, 180 g. of it was added drop by drop to a boiling mixture of 300 cc. of alcohol and 150 g. of zinc dust. The effluent gas was washed, dried and then converted into allene tetrabromide by passing it into an ice-cold solution of bromine in carbon tetrachloride. This was worked up in the usual way by washing, drying and distilling, the fraction boiling at 95–110° (10 mm.) being collected. This fraction was redistilled for the portion which came over at 103–106" and 7 mm.; weight, 70 g. This sample was used for the physical constants.

Preparation from **Dibromo-2,3-propene-1.** Second Method.—The dibromopropene, dissolved in twice its volume of carbon tetrachloride, was placed in a flask fitted

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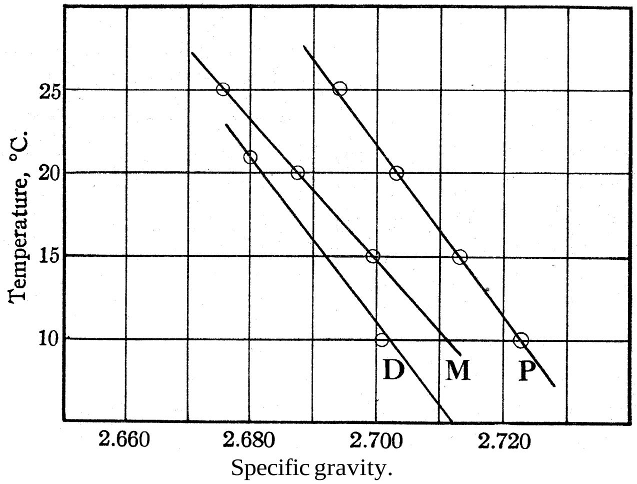
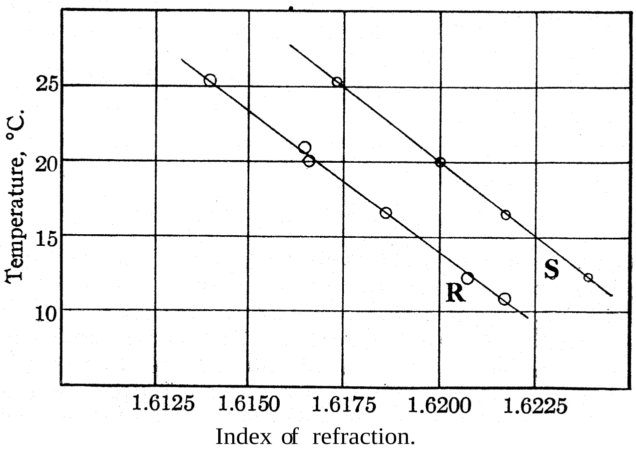
[19] Lespieau and Bourguel, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 49.

with a dropping funnel and a mechanical stirrer. It was cooled by an ice-bath. Bromine was added slowly from the dropping funnel until an equivalent amount had been added. After drying and distillation, the fraction 93–104° (3 mm.) was collected; weight 120 g. Redistillation of this, discarding the first and last portions, gave 84 g. which boiled at 115.5° and 9 mm. This material was solidified by cooling it in an ice-bath. It was allowed to melt slowly, the first portions to melt being discarded. This process was thrice repeated and a sample of allene tetrabromide weighing 60 g. was obtained. This sample was used for determination of the constants.



Methylacetylene tetrabromide: D, results of Demjanov and Dojarenka; M, this investigation. Allene tetrabromide: P, this investigation.

Fig. 2.



R, Allene tetrabromide; S, methylacetylene tetrabromide.

Fig. 3.

In this investigation the melting points were determined by the cooling curve method, using a calibrated and standardized thermometer. It is pertinent to note that the greater purity of the material in the second method was occasioned by the fact that it was prepared in greater quantity and was crystallized several times. The value of 5.5–6° with one crystallization of a portion from a 60-g. sample was found to change to +1.9° when the size of the original preparation was but 17 g. Several fractionations are evidently essential for preparing allene tetrabromide of high purity.

Physical Constants of Allene Tetrabromide

Investigator		Boiling point °C.	Mm.	M. p., °C.	Density d	Temp., °C.	Index of refraction n_D	Temp., °C.
Reboul[20]		250–252	Atm.	...	2.64	...		
Gustavson and Demjanov		215–230 (dec.)	Atm.	−18–0	2.729	0/0		
Gustavson and Demjanov		.....	...	...	2.653	18/0	.....	...
Lespieau		230–250 (sl. dec.)	Atm.	10–11	2.739	0/4	.....	...
Lespieau		169–170	80	...	...	...		
Demjanov and Dojarenka		123–125	17	...	...	...	.....	...
This investigation	First method	104–106	5.5–6	One	2.714[a]	10/4	1.6213	12.6
		.....	...	cryst.	2.704	15/4	1.6194	16.5
		.....	...	5.5–6	2.694	20/4	1.6153	25.0
		.....	...	...	2.684	25/4	.....	...
	Second method	115.5	9	Reptd.	2.723	10/4	1.6238	12.4
		.....	. .	cryst.	2.713	15/4	1.6217	16.4
		.....	...	10.7	2.703	20/4	1.6200	20.0
		.....	...	...	2.694	25/4	1.6173	25.2

[a] Taken in a 12-cc. specific gravity bottle.

Discussion of Data

As with methylacetylene tetrabromide, the Dühring line for allene tetrabromide is plotted in Fig. 1. The observation of Demjanov and Dojarenka fails to conform to the curve. If extrapolated, the boiling point at 760 mm. would be 245°, which is considerably higher than Gustavson and Demjanov's observation, but agrees with Lespieau's and with Reboul's.

The purity of our material used for the physical constants by the second method was evidenced by the sharpness and the constancy of the melting point. The results are considered accurate to 1 part in 3000 for the density, and to one part in the fourth decimal 'place for the refractive index. Lespieau's value for the density at 0° is only slightly lower than the extrapolated value from our curve. Because of the lesser purity of the material prepared by the first method, it has not been included on the chart. The slope of its curve would be identical but the values are lower throughout. So also, in Fig. 3, only the data of the second method have

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[20] Reboul, *Ann. chim. phys.*, [3] **60**, 51 (1860).

been included for the index of refraction curve. The values of the material of lesser purity would give a curve of similar slope and would come between the two curves of allene and methylacetylene tetrabromides. Curiously, however, it is nearer the latter than the former. This shows clearly that index of refraction data, and density data as well, are apt to be quite misleading in these two cases as a means of identification unless *pure* substances are at hand. In other words, a mixture of allene and methylacetylene could not be analyzed even with fair accuracy by conversion to the tetrabromide mixture, if boiling point, density or n_D values are the basis of evaluation. Fortunately, however, their analysis's may be effected readily in another manner.

Summary

Methylacetylene has been prepared in a high state of purity from methyl iodide and sodium acetylide in liquid ammonia. Preparing it by dehalogenation of propylidene chloride is not to be recommended because of poor yields, whereas similar preparation from propylene bromide invariably gives rise to allene as well. Such a mixture cannot be readily separated by fractional distillation, although the percentage of allene was lowered from 5.5 to 1.2 by this means. Methylacetylene tetrabromide was prepared from all three sources, and the physical constants studied.

Allene tetrabromide was made by the addition of bromine either to allene or to dibromo-2,3-propene-1. For purposes of high purity, it must be purified by several crystallizations as well as by fractional vacuum distillation. Such material melts at 10.7°. Boiling point, specific gravity and index of refraction data were obtained.

EVANSTON, ILLINOIS

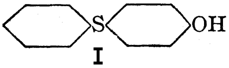
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE SYNTHESIS OF SOME IODATED DIPHENYL-SULFIDE PHENOLS[1]

BY SHAILER L. BASS AND TREAT B. JOHNSON

RECEIVED OCTOBER 16, 1929 PUBLISHED MARCH 6, 1930

In quest of phenolic compounds possessing properties requisite for their practical use in internal antisepsis, Hilbert and Johnson[2] have recently extended the research program of this Laboratory on germicides into the field of the diaryl-sulfide phenols. p-Hydroxydiphenyl-sulfide, I, with its high germicidal value and low toxicity (phenol coefficient 115) has proved the most promising of these derivatives thus far examined.



I

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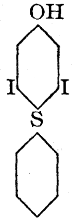
[1] Constructed from a dissertation presented by Shailer L. Bass in June, 1929, to the Faculty of the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Hilbert and Johnson, THIS JOURNAL, 51, 1526 (1929).

It is well known that the substitution of halogen in the benzene nucleus of phenolic compounds leads to derivatives of considerably higher germicidal power than is possessed by the unsubstituted compounds.[3] In order to increase our knowledge of this particular influence or) antiseptic power, we have directed our attention in this research to the study of some iodine derivatives of diphenyl-sulfide phenols. This element is known to function in a manner important to animal metabolism when present in compounds structurally related to tyrosine,[4] as in thyroxine.[5] The latter can be regarded as an a-amino acid derivative of a tetra-iodated *p*-hydroxydiphenyl oxide. The results obtained by Harington[5] lend new interest to the postulation that iodated derivatives of the structurally related *p*-hydroxydiphenyl-sulfide, I, may also possess thyroxine-like activity, or exercise some other specific physiological action of therapeutic value.

Two isomeric di-iododiphenyl-sulfidephenols II and IV and their respective methyl homologs III and V have been synthesized. In order to obtain an indication of the possible effect of substituting halogen in the second benzene ring[6] the compound VI has also been prepared. It is to be noted here that no attention has been paid thus far to thyroxine-like constructions in which the iodine atoms occupy *meta* positions with respect to the hydroxyl group, or unsymmetrical positions in the benzene rings. Also, we have practically no knowledge of the spacial influence of iodine with respect to the hydroxyl group in sulfide phenols upon the antiseptic power of such combinations.



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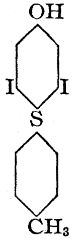

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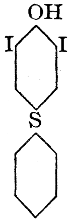

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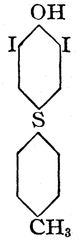

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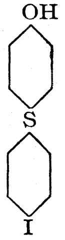

VI

A survey of the chemical literature revealed the fact that only a small number of unsymmetrical halogen derivatives of diphenyl-sulfide had been prepared, and no iodated diaryl-sulfide phenols were known when we began this work. In order to obtain the intermediates desired for the final synthesis of the phenols II and III, 3,4,5-tri-iodonitrobenzene, VII, was

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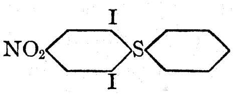
[3] S. Frankel, "Arzneimittel-Synthese," J. Springer, Berlin, 1927, 6th ed., p. 610; Bechold and Ehrlich, Z. *physiol. Chem.*, 47, 173 (1906).

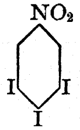
[4] Wheeler and Jamieson, *Am. Chem.* J., 33, 365 (1905); Harington and Randall, *Chem. Ind.*, 48,296 (1929).

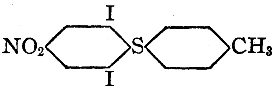
[5] Harington and Barger, *Biochem.* J., 21, 169 (1927).

[6] Cf. "Halogen Derivatives of Benzyl-resorcinol," Klarmann and Von Wowern THIS JOURNAL, 51, 605 (1929).

condensed with sodium thiophenate and sodium *p*-thiocresolate, respectively. This reaction is applied with the greatest success by working in 90% alcohol solution.


VIII


VII


IX

The nitro compounds VIII and IX were reduced with stannous chloride and hydrochloric acid to the corresponding amines. Using these reagents the iodine atoms substituted in the benzene nucleus were not replaced. These amines were so weakly basic that their hydrochlorides were unstable in water and were prepared for our work by passing anhydrous hydrogen chloride into absolute ether solutions of the amines. Diazotization was applied with success by treating the hydrochloride suspended in glacial acetic acid with butyl nitrite. The resulting solutions of the diazonium salts were then diluted with water, and poured slowly into boiling 60% sulfuric acid, when the phenols II and III were formed. Attempts to utilize the Ziegler reaction[7] for the synthesis of iodated sulfide derivatives applicable for the synthesis of the phenols IV and V were without success. The interaction of 2,6-di-iodo-4-amino-anisole-diazonium chloride,[8] for example, with thiophenol in alkaline solution yielded a very stable diazothio-ether. When this latter compound was decomposed, a complex mixture of products was obtained from which diphenyl disulfide, but none of the methyl ether of the phenol IV, could be isolated.

The fact that this type of decomposition can be effected in an anhydrous solvent such as toluene suggests that the reaction does not proceed in accordance with the mechanism proposed by Hantzsch and Freese;[9] that the formation of diphenyl disulfide results from hydrolysis of the diazothio-ether, and the subsequent oxidation of the thiophenol by the air. When p-anisidine diazonium chloride solution is allowed to interact with an alkaline solution of thiophenol, the diazothio-ether is so unstable that it cannot be isolated. Decomposition leads to the formation of *p*-methoxy-diphenyl-sulfide,[2] which can easily be demethylated to form the phenol I.

The great difference in the stability and the character of the decomposition of these two very similar diazothio-ethers may be explainable by the structural relation between the nitrogen and the sulfur atoms as expressed by Hantzsch and Freese's[9] "anti" and "syn" forms. Theoretically the "syn" form should readily yield sulfides. However, the reaction between diazonium salts and mercaptans in alkaline solution is practically instan-

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[7] Ziegler, Ber., 23, 2469 (1890).

[8] Kalb, Schweizer, Zellner and Berthold, ibid., 59, 1869 (1926).

[9] Hantzsch and Freese, *ibid.*, 28, 3237 (1895).

taneous, so that diazothio-ethers may also exhibit the type of structural isomerism postulated by Hantzsch[10] for the diazonium salts. More work must be done upon the structure of the diazonium salts and their diazothio-ethers before this point can be decided finally.

The two *ortho*-di-iodated phenols, IV and V, were obtained by iodation of *p*-hydroxy-diphenyl sulfide I and the corresponding *p*-hydroxy-*p'*-methyl-diphenyl sulfide, respectively. The method of Datta and Prosad,[11] as modified by Harington,[12] was used. Iodine in potassium iodide solution was added to a warm solution of the diphenyl sulfide phenol in a large quantity of concentrated ammonia which contained ammonium sulfate. Under these conditions the hydroxyl group directed the entering halogen atoms instead of the sulfur atom as in all previous experiments on the halogenation of aromatic sulfides.[13] Iodation in the cold, however, or in ammonium hydroxide solutions containing methyl alcohol as a solvent resulted in the formation of a large amount of tar insoluble in dilute sodium hydroxide.

On account of the extreme insolubility of our iodated sulfide phenols in water, they did not exhibit any pronounced bactericidal properties. Saturated solutions of all five iodated compounds in water, 5 or 20% alcohol solutions, were without effect on *Bact. typhosum*, as compared with phenol in the same solvents. The pharmacological properties of these compounds, in particular the thyroxine-like action, will be investigated. Other halogenated compounds of this series will also be examined and their pharmacological properties determined.

Experimental Part

4-Nitro-2,6-di-iodo-diphenylsulfide, VIII.—Twenty grams of 3,4,5-tri-iodo-nitrobenzene[5,8] was suspended in 800 cc. of boiling 90% alcohol and a solution containing one equivalent of sodium thiophenate added. The latter was prepared by adding 0.92 g. of sodium to 4.4 g. of thiophenol in 50 cc. of alcohol. The tri-iodonitrobenzene rapidly dissolved and the solution acquired a light orange color. After heating under a reflux condenser for five hours, one-half of the alcohol was distilled off and the hot solution then diluted with water. On cooling, an 86% yield of the pure nitro compound was obtained. Two crystalline modifications were observed; canary-yellow needles separated from warm 90% acetic acid solution, but slowly redissolved and separated on further cooling as orange rhomboids. Both forms melt at 105.5° and their mixture also melts at this temperature.

Anal. Calcd. for $C_{12}H_7O_2NSI_2$: I, 52.56; S, 6.64. Found: I, 53.1, 53.1; S, 6.74, 6.67.

4-Nitro-2,6-di-iodo-phenyl-*p*-tolylsulfide, M.—This sulfide was prepared in a

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[10] Hantzsch and Reddelien, "Die Diazoverbindungen," J. Springer, Berlin, 1921.

[11] Datta and Prosad, THIS JOURNAL, **39**, 441 (1917).

[12] Harington, *Biochem. J.*, **22**, 1429 (1928).

[13] Boeseken, *Rec. trav. chim.*, **29**, 322 (1910); Fries and Vogt, *Ann.*, **381**, 337 (1911). See also Krafft, *Ber.*, **7**, 1165 (1874); Loth and Michaelis, *ibid.*, **27**, 2547 (1894); Blanksma, *Rec. trav. chim.*, **20**, 402 (1900); Bourgeois, *Ber.*, **28**, 2321 (1895).

manner similar to its lower homolog; the yield was 83% of the theoretical. Here again two crystalline modifications were observed. Fan-shaped aggregates of light yellow needles crystallized from alcohol, but redissolved and crystallized, on cooling, as yellow rhomboids. Both forms melted at 121–122° with preliminary softening at 120°.

Anal. Calcd. for $C_{13}H_9O_2NSI_2$: I, 51.08; S, 6.45. Found: I, 51.1, 50.1; S, 6.4, 6.2.

4-Amino-2,6-di-iodo-diphenylsulfide.—Ten grams of the nitro compound, VIII was reduced by digesting for two hours with 26 g. of stannous chloride and 30 cc. of hydrochloric acid (sp. gr. 1.16) in 250 cc. of alcohol. After evaporating the resulting solution under diminished pressure, the sirupy residue was dissolved in water and treated with an excess of a 10% solution of sodium hydroxide. The precipitate was filtered by suction and the amine extracted with boiling alcohol; the solution was decolorized with norite and then diluted with water. On cooling, colorless prisms deposited which melted at 146°. The yield was 70%.

Anal. Calcd. for $C_{12}H_9NSI_2$: I, 56.04; S, 7.08. Found: I, 56.9, 57.0; S, 6.4, 7.0.

The hydrochloride was obtained by passing dry hydrogen chloride into an ether solution of the amine. It melted at 192" with decomposition.

4-Amino-2,6-di-iodo-phenyl-*p*-tolylsulfide.—This was obtained by reduction of the nitro compound IX with stannous chloride. The amine was obtained as colorless lance-shaped crystals which melted at 197–198". The yield was 70% of the theoretical.

Anal. Calcd. for $C_{13}H_{11}NSI_2$: I, 54.36; S, 6.87. Found: I, 53.4, 53.6; S, 6.9, 6.8.

The hydrochloride of this base melts at 182' with decomposition.

4-Hydroxy-2,6-di-iodo-diphenyl-sulfide, 11.—Nine grams of the hydrochloride of 4-amino-2,6-di-iodo-diphenyl-sulfide was suspended in 50 cc. of glacial acetic acid and diazotized at 5–10' by interaction with 3 g. of n-butyl nitrite in 25 cc. of glacial acetic acid. The deep red solution of the diazonium salt was diluted with an equal volume of water and added slowly to 200 cc. of a mixture of equal volumes of concentrated sulfuric acid and water. The reaction solution was maintained at 135–140° during this operation. The phenol was separated from the tarry product resulting from this reaction by extraction with a mixture of 20% sodium hydroxide and alcohol. The alcoholic layer was filtered and the filtrate saturated with carbon dioxide; the solution was filtered and then acidified with hydrochloric acid. The colorless oil that separated was dissolved in dilute alcohol, from which the phenol crystallized in long prisms. A yield of 3.4 g. was obtained. The crystals contained one molecule of alcohol of crystallization (9.4%) and rapidly disintegrated to a white powder when exposed to the air. The crystals did not melt but dissolved in their alcohol of crystallization at 92–95'. The powder melted at 139°.

Anal. Calcd. for $C_{12}H_8O_5I_2$: I, 55.9; S, 7.06. Found: I, 56.9; S, 7.0.

4-Hydroxy-2,6-di-iodo-phenyl-*p*-tolyl-sulfide, III.—Six grams of the above amine hydrochloride were diazotized with butyl nitrite and the solution of the diazonium salt poured into one liter of cold absolute ether. The red-brown powder which separated was filtered off, suspended in ice water and finally added to the boiling sulfuric acid. The phenol formed was extracted as described above and was obtained in a yield of 25%. It crystallized from dilute alcohol in needles which melted at 154°. It is soluble in dilute sodium hydroxide solution, and dissolves in boiling 5% alcohol to the extent of 1:20,000, but on cooling crystallizes from dilutions as high as 1:80,000.

Anal. Calculated for $C_{13}H_{10}OSI_2$: I, 54.24; S, 6.85. Found: I, 54.7, 55.0; S, 6.7, 6.8.

4-Methoxy-3,5-di-iodobenzene-diazo-thiophenyl Ether.—Ten grams of **di-iodo-*p*-anisidine,**[8] dissolved in 200 cc. of 40% alcohol and 120 cc. of hydrochloric acid (sp. gr.

1.16) was diazotized at 0° by interaction with sodium nitrite. After adding urea and sodium acetate, the solution was added slowly with stirring to a solution of 3 g. of thiophenol and 40 g. of sodium hydroxide in 500 cc. of water, keeping the temperature below 80°. A yellow precipitate of the above diazo compound was obtained. This was filtered and washed with dilute sodium hydroxide and with water, and finally dried in vacuo over calcium chloride. The yield was nearly the theoretical. The compound crystallizes from alcohol in yellow plates which melt sharply at 91° with evolution of nitrogen.

Anal. Calcd. for $C_{13}H_{10}OSN_2I_2$: I, 51.16; S, 6.46; N, 5.65. Found: I, 51.2; S, 6.2; N, 5.9.

Attempts to convert this diazo compound into 4-methoxy-3,5-di-iodo-phenyldisulfide were unsuccessful. Only viscous oils were obtained by heating from which no sulfide could be obtained in a pure condition.

Formation of **3,5-Di-iodo-4-hydroxydiphenyl-sulfide,** IV, by Iodation of ***p*-Hydroxyphenyl Sulfide,** I.—Ten grams of *p*-hydroxy-diphenyl-sulfide I were dissolved in 450 cc. of aqueous ammonia (sp. gr. 0.9) and combined at 35–40° with 65 cc. of 2.5 *N* iodine solution. The ammonium salt of the di-iodated phenol separated in the form of colorless needles mixed with considerable tarry material. The reaction product was separated by filtration, acidified to liberate the free phenol, the latter extracted from the tar by trituration with dilute sodium hydroxide and the alkaline solution decolorized with norite. On saturating the alkaline solution with carbon dioxide the phenol separated and was crystallized from dilute methyl alcohol. It crystallized in long prisms which melted at 84–85". The yield was 7.5 g. It is extremely soluble in the common organic solvents and is very insoluble in water.

Anal. Calcd. for $C_{12}H_8OSI_2$: S, 55.92; I, 7.06. Found: S, 55.8; I, 6.8.

3,5-Di-iodo-4-hydroxy-4′-methyl-diphenyl-sulfide, V, by Iodation of ***p*-Hydroxy-*p*′-methyl-diphenyl Sulfide.**[2]—This compound crystallizes from dilute methyl alcohol in clusters of colorless needles which melt at 112–113".

Anal. Calcd. for $C_{13}H_{10}OSI_2$: S, 54.2; I, 6.85. Found: S, 54.6; I, 6.90.

By application of the technique described in the preceding preparations, the following compounds were also prepared (Table I).

TABLE I

RESULTS OF PREPARATIONS

No.	-Diphenyl sulfide	Formula	M. p., °C.	Yield. %	Analyses	S, %
1	*p*-Methoxy-*p*′-nitro-[a]	$CH_3OC_6H_4SC_6H_4NO_2$	71	92	.....	12.00[15]
2	*p*-Methoxy-*p*′-amino-[b]	$CH_3OC_6H_4SC_6H_4NH_2$	96	80	N, 6.38	13.5
3	*p*-Methoxy-*p*′-iodo-[c]	$CH_3OC_6H_4SC_6H_4I$	102	68	I, 37.2	9.0
4	*p*-Hydroxy-*p*′-iodo-(VI)[d]	$HOC_6H_4SC_6H_4I$	111–112	51	I, 38.4	9.30

[a] From $CH_3OC_6H_4SNa$[14] and $NO_2C_6H_4Cl$. Purified by crystallization from alcohol. [b] By reduction of the nitro compound with stannous chloride and hydrochloric acid in alcohol. The hydrochloride melts at 205–207°. [c] B. p., 202–205" at 3–4 mm. crystallized from methyl alcohol. [d] By demethylation of the methyl ether according to Hilbert and Johnson's procedure.[2] B. p., 205–210° at 3 4 mm. Crystallized from methyl alcohol. Solubility in water, 1:14000 at 100°.

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[14] Prepared in 72% yield from *p*-anisidine by the method of Leuckart, *J. prakt. Chem.*, 41, 179 (1890).

[15] Carius method as modified by Rogers and Dougherty, THIS JOURNAL, 50, 1231 (1928).

Summary

1. Five new iodine derivatives of p-hydroxydiphenyl-sulfide have been described, namely: 4-hydroxy-2,6-di-iododiphenyl-sulfide, 4-hydroxy-2,6-di-iodo-4'-methyl-diphenyl-sulfide, 4-hydroxy-3,5-di-iododiphenyl-sulfide, 4-hydroxy-3,5-di-iodo-4'-methyldiphenyl-sulfide and 4-hydroxy-4'-iododiphenyl-sulfide.

2. All of these phenols are characterized by their extreme insolubility in water; consequently they do not exhibit any bactericidal activity when tested in the usual way.

3. The study of phenolic derivatives of diphenylsulfide will be continued.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON PYRIMIDINES. CXIII. AN IMPROVED METHOD FOR THE SYNTHESIS OF CYTOSINE[1]

BY GUIDO E. HILBERT[2] AND TREAT B. JOHNSON

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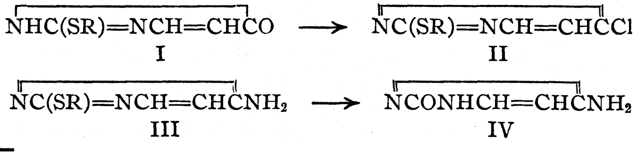
The pyrimidine—cytosine—was first isolated from a nucleic acid by Kossel and Neumann[3] in 1894. It was subsequently synthesized by Wheeler and Johnson[4] and the structure of this naturally occurring compound thereby definitely established.

The successful synthesis developed by Wheeler and Johnson involves the condensation of a pseudothiourea with the sodium salt of ethyl formylacetate, resulting in the formation of a 2-mercapto-G-oxypyrimidine, I. By interaction of this cycle with phosphorus pentachloride, the corresponding 2-mercapto-6-chloropyrimidine, II, is formed, which is finally converted into the corresponding aminopyrimidine, III, by the action of ammonia. This latter pyrimidine, when digested with hydrochloric acid, is changed almost quantitatively into the hydrochloride of cytosine, IV. These various changes are expressed by the following formulas

$$RSC(NH_2){=}NH + NaOCH{=}CHCOOC_2H_5 \longrightarrow$$



$$\underset{\text{I}}{NHC(SR){=}NCH{=}CHCO} \longrightarrow \underset{\text{II}}{NC(SR){=}NCH{=}CHCCl}$$

$$\underset{\text{III}}{NC(SR){=}NCH{=}CHCNH_2} \longrightarrow \underset{\text{IV}}{NCONHCH{=}CHCNH_2}$$

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[1] A preliminary report of this research was given at the Spring Meeting of the American Chemical Society held in Columbus, Ohio, in April, 1929.

[2] Sterling Research Fellow 1928–1929.

[3] Kossel and Neumann, *Ber.*, 27,2215 (1894).

[4] Wheeler and Johnson, *Am.* Chem. J., 29,492, 505 (1903).

Notwithstanding the fact that the technique of this method of synthesis is difficult for an inexperienced worker to apply, it is the only one of practical interest recorded in the literature that has served to make this pyrimidine available in quantity for experimental work. A serious objection to the procedure, however, is the evolution of mercaptan, which is necessarily formed during the last hydrolysis change with acids when cytosine IV is formed. We have now developed a new method of operating which not only eliminates the use of sulfur compounds but also simplifies the technique of the synthesis.

The improved method for obtaining uracil, V, synthetically which was developed by Davidson and Baudisch[5] has opened up a new approach to many important derivatives of this oxypyrimidine. They have shown that uracil can be obtained in good yield by condensing urea with malic acid in the presence of fuming sulfuric acid. By applying this excellent method of synthesis and using uracil V as the starting point of our work, we have now succeeded in developing a new and practical procedure for obtaining cytosine IV easily. In fact, our method of operating permits of the preparation of both cytosine IV and isocytosine VI directly from uracil V.

$$\mathrm{HOOCCH_2CH(OH)COOH + NH_2CONH_2}$$

$$\mathrm{NHCONHCH{=}CHCO} \qquad \mathrm{NHC(NH_2){=}NCH{=}CHCO}$$

V VI

By allowing 2,6-dichloropyrimidine, VII, to interact with ammonia in alcohol solution at 100°, Gabriel[6] obtained a mixture of the two isomeric pyrimidines represented by formulas VIII and IX, respectively. A partial separation of these two compounds was effected by fractional crystallization from ethyl acetate, but a yield of 15% only of 2-chloro-6-aminopyrimidine (m. p. 206–207°) IX was obtained. The remaining fraction was designated as 2-amino-6-chloropyrimidine, VIII, and was obviously highly impure, being contaminated with its isomer. Wheeler[7] later prepared these two isomers in an impure state and examined the behavior of a mixture on reduction. By digestion in water with zinc dust he found 2-amino-6-chloropyrimidine, VIII, to be reduced to 2-aminopyrimidine, while 2-chloro-6-aminopyrimidine, IX, was not changed by the treatment.

We have repeated the work of Gabriel and find that the reaction between 2,6-dichloropyrimidine, VII, and ammonia takes place smoothly at ordinary temperature. The yield of 2-chloro-6-aminopyrimidine, IX, and 2-amino-6-chloropyrimidine, VIII, obtained is about 40 and 60%, respectively. Attempts to separate these isomers by fractional crystallization from various solvents proved unsatisfactory. Purification was finally

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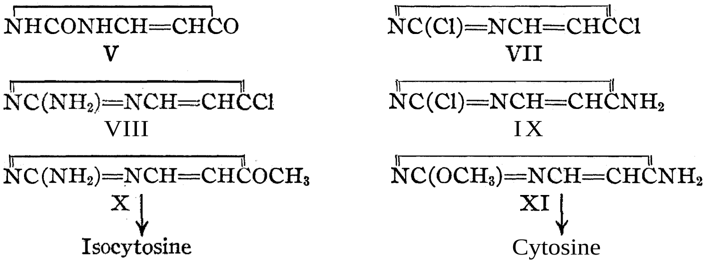
[5] Davidson and Baudisch, This Journal, 48, 2379 (1926).

[6] Gabriel, *Ber.*, 38, 1689 (1905).

[7] Wheeler, *J. Biol. Chem.*, 3, 288 (1907).

effected by means of steam distillation, 2-amino-6-chloropyrimidine, VIII, distilling easily, whereas its isomer remained behind. Unfortunately, secondary reactions take place during steam distillation which reduce the yields. The chlorine atom in 2-amino-6-chloropyrimidine, VIII, is much more reactive, as Wheeler observed, than the chlorine in the isomeric form, IX. This was shown by the difference in behavior of the two compounds toward the Wheeler and Johnson color test.[8] The former, VIII, gave a positive color test characteristic for isocytosine, while the isomer, 2-chloro-6-aminopyrimidine, IX, failed to give a corresponding reaction. The behavior on hydrolysis also revealed the difference in reactivity of the chlorine atom in these respective isomers. On heating with water 2-amino-6-chloropyrimidine, VIII, gave isocytosine, whereas the 2-chloro-6-aminopyrimidine, IX, failed to react. Hydrolysis of the latter to cytosine was brought about, however, by heating with water at 140°. The partial destruction of the chloro-aminopyrimidine with formation of uracil made it impossible, however, to obtain cytosine by this method in good yields.

A satisfactory method for preparing cytosine was finally developed by first transforming the chloro-aminopyrimidines into their corresponding methoxy derivatives by interaction with sodium methylate. The resulting isomeric methyl ethers were easily separated by fractional crystallization from hot water, in which 2-amino-6-methoxypyrimidine, X, is extremely soluble. By this method we were able to obtain consistently yields of 2-methoxy-6-aminopyrimidine, XI, from 2,6-dichloropyrimidine, VII, corresponding to 40% of the theoretical. When this pyrimidine, XI, was warmed on the steam-bath with hydrochloric acid, practically a quantitative yield of cytosine hydrochloride was obtained. The various transformations discussed above are expressed by the following formulas.



$\overline{\text{NHCONHCH=CHCO}}$ V

$\overline{\text{NC(Cl)=NCH=CHCCl}}$ VII

$\overline{\text{NC(NH}_2\text{)=NCH=CHCCl}}$ VIII

$\overline{\text{NC(Cl)=NCH=CHCNH}_2}$ IX

$\overline{\text{NC(NH}_2\text{)=NCH=CHCOCH}_3}$ X $\downarrow$ Isocytosine

$\overline{\text{NC(OCH}_3\text{)=NCH=CHCNH}_2}$ XI $\downarrow$ Cytosine

Experimental Part

Preparation of **2,6-Dichloropyrimidine, VII.**—A yield of this pyrimidine corresponding to 50% of the theoretical was obtained by Johnson and Menge[9] by interaction of 2-thiouracil with phosphorus pentachloride. Gabriel6 obtained this pyrimidine in a

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[8] Wheeler and Johnson, *J. Biol. Chem.*, **3**, 183 (1907).

[9] Johnson and Menge, *ibid.*, 2,115 (1906).

yield of 80% by heating uracil with phosphorus oxychloride under pressure at a temperature of 140°. He worked with very small quantities of uracil *(2.5 g.)*, and his technique is not suitable for preparing the dichloropyrimidine from uracil in quantity. We recommend the following procedure for the preparation of this compound.

One hundred grams of uracil, prepared according to the method of Davidson and Baudisch,[5] is suspended in 400 cc. of phosphorus oxychloride and the mixture heated at 110–120° for five hours. The uracil rapidly dissolves with evolution of hydrochloric acid, yielding a dark brown homogeneous solution. After removing the excess of phosphorus oxychloride by distillation under diminished pressure, 750 g. of crushed ice is then gradually added to the dark-colored viscous residue. The temperature of the reaction mixture was not allowed to rise above 20° during this treatment because of the ease of hydrolysis of the dichloropyrimidine to uracil. During the addition of the ice, ether was also added to facilitate the decomposition of a complex phosphorus compound which was present. The pyrimidine is slightly basic, forming a hydrochloride very soluble in ether. After removing the ether layer, the strongly acid solution was repeatedly extracted with ether and the combined extracts washed with sodium carbonate solution and finally dried over calcium chloride. After removal of the ether the dichloropyrimidine was then purified by distillation. It boiled at 203° (uncorr.) and solidified on cooling, melting at 61°. A yield of 90 g. was obtained equivalent to 68% of the theoretical. The pyrimidine is a strong lachrymator and has an irritating effect on the skin.

Interaction of **2,6-Dichloropyrimidine** with Ammonia. The Formation of 2-Amino-6-chloropyrimidine, VIII, and 2-Chloro-6-aminopyrimidine, **IX.**—This chloride reacts with ammonia at ordinary temperature. Forty grams of the pulverized dichloropyrimidine is dissolved in 300 cc. of absolute alcohol previously saturated with ammonia gas and the solution preserved in a stoppered bottle. The reaction starts almost immediately and after standing for an hour the solution warms up appreciably and a crystalline solid commences to separate from the alcohol. After allowing to stand for about eighteen hours the solid material is filtered off and the alcohol filtrate evaporated to expel the excess of alcohol and ammonia and recover dissolved pyrimidines. The total reaction product is washed thoroughly with cold water to remove ammonium chloride and then dried. We obtained 33 g. of the mixed chloro-aminopyrimidines, corresponding to a yield of 95% of the theoretical.

Of the various methods applied for separating the two isomeric chloro-aminopyrimidines, the following was as satisfactory as any thus far reported. Thirty-three grams of the mixed pyrimidines was suspended in 200 cc. of water made alkaline with 15 cc. of concentrated ammonia and then subjected to steam distillation. The 2-amino-6-chloropyrimidine distilled over as a colorless solid and was obtained in a pure state after one crystallization from alcohol. The yield was 4.0 g. In order to obtain the isomeric 2-chloro-6-aminopyrimidine, the hot aqueous solution was filtered free from a small amount of flocculent impurity and then chilled, when the pyrimidine separated in a crystalline condition and was further purified by crystallization from hot water. The yield obtained was 10 g. As indicated by the yields obtained, over 50% of the original mixture of pyrimidines is destroyed by the treatment with steam. In fact, in one experiment a considerable proportion of the 2-chloro-6-amino-pyrimidine was converted into cytosine.

2-Amino-6-chloropyrimidine, **VIII.**—This crystallizes from alcohol in glistening plates which turn brown on heating and decompose at 168°. Gabriel and Colman[10] prepared the pyrimidine by treatment of isocytosine with phosphorus oxychloride. This pyrimidine responds to the Wheeler and Johnson color test for isocytosine and forms an

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[10] Gabriel and Colman, Ber., 36, 3383 (1903).

insoluble picrate which decomposes at an indefinite temperature (270°), depending on the rate of heating.

Anal. Calcd. for $C_4H_4N_3Cl$: Cl, 27.39. Found: Cl, 27.27, 27.34.

This pyrimidine is formed almost exclusively when 2,6-dichloropyrimidine is warmed with concentrated aqueous ammonia at 50°.

2-Chloro-6-minopyrimidine, IX.—This pyrimidine crystallizes from hot water in long needles melting with decomposition at 219–220°. The compound is somewhat more soluble in water and alcohol than its isomer. Unlike 2-amino-6-chloropyrimidine, it does not respond to the Wheeler and Johnson color test.

Anal. Calcd. for $C_4H_4N_3Cl$: Cl, 27.39. Found: Cl, 27.69, 27.49.

Formation of **Isocytosine.**—One gram of 2-amino-6-chloropyrimidine was refluxed with 60 cc. of water for twenty hours. The solution had then assumed a yellow color and was strongly acid to litmus. After adding ammonia to neutralize hydrochloric acid, the solution was concentrated to a volume of about 20 cc. and allowed to cool slowly, when stout prisms of isocytosine separated. They melted at 280° with decomposition, were free from chlorine and responded to the Wheeler and Johnson color test characteristic for isocytosine. Aqueous solutions of this base have a tendency to gel when cooled quickly. It is also of interest to mention here that a solution of this pyrimidine supports the growth of a mold when exposed to the air.

Formation of Cytosine.—Four grams of 2-chloro-6-aminopyrimidine was heated with 20 cc. of water at 140° for two hours. A clear solution was obtained which was acid to litmus. After making slightly alkaline with ammonia and cooling in an ice-bath, a mixture of cytosine and uracil separated. This was separated by filtration, treated with dilute hydrochloric acid to separate the uracil and the acid solution made alkaline with ammonia and cooled. The cytosine separated in crystalline condition and was further purified by crystallization from hot water. The total yield was equal to 85% of the theoretical. The base contained one molecule of water of crystallization, which was lost by heating at 100°.

Anal. Calcd. for $C_4H_5ON_3 \cdot H_2O$: H_2O, 13.95; N, 37.84 (anhydrous base). Pound: H_2O, 13.96; N, 37.74 (anhydrous base).

2-Chloro-6-aminopyrimidine was recovered unchanged after refluxing a water solution for twenty hours. After heating with water for several hours at 190° a mixture of cytosine and uracil was obtained, the uracil predominating.

Conversion of the Aminochloropyrimidines, VIII and IX, into Their Corresponding Methoxypyrimidines, X and XI

2-Methoxy-6-aminopyrimidine, XI.—A solution of 57 g. of a mixture of the isomeric pyrimidines (VIII and IX) in 700 cc. of dry methyl alcohol was combined with a methyl alcohol solution containing 12 g. of sodium and the mixture refluxed for six hours. Sodium chloride separated immediately and within a short time the reaction was complete. After filtering from sodium chloride, the solution was concentrated to a volume of 100 cc. and cooled, when the above pyrimidine separated in a practically pure form. It crystallized in the form of needles which melted at 173°. The yield was 16.5 g. The alcohol filtrate was then evaporated to dryness in a blast of dry air and the residue, weighing 35 g., dissolved in boiling water; the solution was chilled after decolorizing with norite. Eight grams more of the above pyrimidine separated. On recrystallizing all our product from water, we obtained 22 g. or about 40% of a theoretical yield. This pyrimidiie crystallizes in bundles of colorless prisms which shrivel in a capillary tube at 169° and melt at 174°.

Anal. Calcd. for $C_5H_7ON_3$: N, 33.60. Found: N, 33.69, 33.50.

2-Amino-6-methoxypyrimidine, **X.**—This pyrimidine is recovered from the above aqueous filtrates from which the 2-methoxy-6-aminopyrimidine has been separated. This compound has previously been described by Gabriel and Colman,[10] who have shown that it is converted to isocytosine by hydrolysis with hydrochloric acid.

A practically quantitative yield of 2-amino-6-methoxypyrimidine is formed by treatment of 2-amino-6-chloropyrimidine with sodium methylate. It crystallizes from water in the form of colorless prisms which melt at 125° to an oil. After sublimation the melting point was raised to 125–126°. An attempt to separate and purify the two isomeric methoxypyrimidines, X and XI, by fractional sublimation was unsuccessful.

Formation of Cytosine by Hydrolysis of 2-Methoxy-6-aminopyrimidine, XI.—Five grams of this pyrimidine was dissolved in concentrated hydrochloric acid and the solution then evaporated to dryness by heating on a steam-bath. The crude hydrochloride of cytosine was dissolved in water, the solution clarified by filtration and finally made alkaline with ammonia. The free base was thereby precipitated in a crystalline condition and was purified by crystallization from hot water, separating in large colorless plates. The product was identical in all respects with cytosine prepared from 2-chloro-6-aminopyrimidine. The yield was quantitative.

Anal. Calcd. for $C_4H_5ON_3 \cdot H_2O$: H_2O, 13.95; N, 37.84 (anhydrous base). Found: H_2O, 14.00; N, 37.61, 38.1 (anhydrous base).

Summary

1. An improved method for the preparation of 2,6-dichloropyrimidine is described.

2. A further study has been made of the chemical properties of the two isomers—2-chloro-6-amino- and 2-amino-6-chloropyrimidine.

3. The isomeric 2-methoxy-6-amino- and 2-amino-6-methoxypyrimidines have been synthesized. Both pyrimidines are transformed quantitatively into cytosine and isocytosine, respectively, when warmed in aqueous solution with hydrochloric acid.

4. The new method developed for the preparation of cytosine directly from uracil is an improvement over the older method of Wheeler and Johnson which involves the use of pseudothioureas.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, PRINCETON, UNIVERSITY]

THE NON-CATALYTIC POLYMERIZATION AND HYDROGENATION OF ETHYLENE[1]

BY ROBERT N. PEASE

RECEIVED OCTOBER 22, 1929 PUBLISHED MARCH 6, 1930

There is now ample evidence that the only primary reaction involved in the vapor-phase cracking of the gaseous saturated aliphatic hydrocarbons (excepting methane) up to at least 650° and in the absence of catalysts is a homogeneous unimolecular dissociation yielding mono-olefins and saturated hydrocarbons of lower molecular weight, or hydrogen. The products of this primary action may, however, suffer further change. The lower hydrocarbons may themselves dissociate. The olefins may polymerize or dissociate. They may also react with any hydrogen which has been formed. The so-called "pyrolysis" of the original hydrocarbon may therefore yield a complex of products. As a further step in the unravelling of the chemical changes involved in this process, some investigation of the behavior of olefins is called for. In this connection we have undertaken a preliminary study of the thermal reactions of ethylene, the results of which are here reported.

Method.—Experiments were conducted mainly by the flow method at atmospheric pressure, though one series of static determinations was carried out. The gases—ethylene, hydrogen and nitrogen, all of high purity—passed through resistance-tube flowmeters and calcium chloride tubes into a pyrex reaction tube which was heated in an electric tube-furnace. The off-gas was collected over mercury and analyzed for higher olefins by absorption in ordinary concentrated sulfuric acid, for ethylene by absorption in dilute bromine water, and for hydrogen and saturated hydrocarbons by fractional combustion with copper oxide. Qualitative tests for acetylene were conducted with ammoniacal cuprous chloride, and showed at most the barest traces of this gas under any conditions studied.

Results

Ethylene Alone.—The behavior of pure ethylene at 1 atm. was investigated by the flow method between 450 and 600°. Data are presented in Table I. The results indicate that the only important reaction at the lower temperatures is the formation of a butylene

$$2C_2H_4 \longrightarrow C_4H_8$$

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[1] This paper contains the results of an investigation carried out as part of Project No. 7 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund donated by Mr. John D. Rockefeller. This fund is being administered by the American Petroleum Institute with the cooperation of the Central Petroleum Committee of the National Research Council. Professor Hugh S. Taylor of Princeton University is Director of Project No. 7.

This conclusion is based on the fact that one volume of gas absorbable by ordinary concentrated sulfuric acid is formed for every two volumes of ethylene disappearing. Above 525°, ethane, methane, a little hydrogen and liquid products begin to appear. The formation of ethane is about in proportion to the amount of ethylene reacting, and this substance is consequently regarded as a primary product. Its amount is never large, and passes through a maximum at 575–600°. Methane is formed at an increasing rate as the heating time is increased, which suggests that it is a secondary product. These data are in general agreement with those of Day,[2] of Hague and Wheeler[3] and of Frey and Smith.[4]

TABLE I

REACTION OF ETHYLENE AT 450–600° AND 1 ATM.

Reaction-tube volume, 637 cc.

Temp., °C.	Gas flow, cc./min.	C_2H_4, cc. In	Out	Reacted	Formed, cc. "C_nH_{2n}"	C_2H_6	CH_4	H_2
450	40	100	95	5	2	2	2	2
	20	100	93	7	3	1	1	1
	10	100	90	10	4	2	2	2
	5	100	85	15	7	1	1	1
475	40	100	94	6	3	1	1	1
	20	100	90	10	4	1	1	1
	10	100	86	14	6	1	1	1
	5	100	78	22	9	3	3	3
500	40	100	92	8	4	2	2	2
	20	100	86	14	6	2	2	2
	10	100	81	19	8	4	4	4
525	40	100	91	9	4	1	1	1
	20	100	83	17	7	3	3	3
	10	100	72	28	9	7	7	7
550	40	100	83	17	6	4	1	1
	20	100	72	28	8	5	4	1
	10	100	58	42	9	8	7	2
575	40	100	77	23	7	6	2	1
	20	100	60	40	9	10	6	2
	10	100	48	52	7	12	13	3
600	40	100	66	34	7	5	9	2
	20	100	53	47	7	9	12	3
	10	100	40	60	7	11	22	3

The kinetics of the low temperature reaction are peculiar. The flow experiments show that the rate falls off rapidly as the heating time is increased (*i. e.*, the flow-rate is decreased) and the temperature coefficient is rather small. These might be characteristics of a contact action occurring at the reaction tube walls. To test this point, experiments by the static

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[2] Day, Am. Chem. *J.*, 8, 153 (1886).

[3] Hague and Wheeler, *J. Chem. Soc.*, 391 (1929).

[4] Frey and Smith, *Ind. Eng. Chem.*, 20, 948 (1928).

method (pressure decrease at constant volume) were carried out by Mr. Paul R. Chesebro. Rates in an empty pyrex tube were compared with rates in a tube packed with broken pyrex glass. If a wall reaction were occurring, the rates in the packed tube would be the greater. Actually the pressure drop was definitely more rapid in the empty tube. Data are given in Table II.

TABLE II

STATIC EXPERIMENTS IN EMPTY AND PACKED PYREX BULB

Temp., °C.	Time, min.	Pressure, mm.	A P per 10 min.	Pressure, mm.	A P per 10 min.
		Empty Bulb		Packed Bulb	
400	0	746	4	775	3
	10	742	4	772	3
	20	738	4	769	4
	30	734	3	765	2
	40	731	4	763	2
	50	727	3	761	1
	60	724		760	
450	0	799	19	788	14
	10	780	12	774	6
	20	768	9	768	7
	30	759	10	761	5
	40	749	7	756	6
	50	742	8	750	6
	60	734		744	
500	0	788	36	775	23
	10	752	24	752	12
	20	728	19	740	11
	30	709	18	729	10
	40	691	13	719	10
	50	678	11	709	11
	60	667		698	

Wall material has therefore a depressing action on the reaction. Similar though more marked effects have been observed in the oxidation of hydrogen[5] and of hydrocarbons,[6] and have been attributed to the occurrence of a homogeneous chain-type reaction in the empty tube, which reaction is suppressed by the packing. A similar explanation will serve in the case of ethylene. Since the effect is not great, it is concluded that either the glass is relatively inefficient in the case of ethylene or that the chains are not long (*i.* e., chain propagation is not efficient). There is, however, no question but that a negative surface action predominates.

Further evidence of the unusual nature of the reaction was obtained from a set of static experiments carried out in the empty bulb. These are summarized in Table III.

[5] Hinshelwood and Thompson, *Proc. Roy. Soc. London,* **118A,** 170 (1928).

[6] Pease, THIS JOURNAL, 51, 1839 (1929).

TABLE III

STATIC EXPERIMENTS AT 400, 450 AND 500° (EMPTY BULB)

Temp., °C.	Time, min.	Pressure, mm.	A P per 10 min.	Pressure. mm.	A P per 10 min.	Pressure, mm.	A P per 10 min.
400	0	602	4	746	4	899	9
	10	598	3	742	4	890	8
	20	595	3	738	4	882	6
	30	592	2	734	3	876	4
	40	590	3	731	4	872	a
	50	587	3	727	3	868	3
	60	584		724		865	
450	0	588	5	799	19	901	22
	10	583	6	780	12	879	17
	20	577	4	768	9	862	12
	30	573	5	759	10	850	10
	40	568	4	749	7	840	9
	50	564	5	742	8	831	9
	60	559		734		822	
500	0	582	15	788	36	910	40
	10	567	12	752	24	870	26
	20	555	9	728	19	844	21
	30	546	8	709	18	823	19
	40	538	8	691	13	804	16
	50	530	6	678	11	788	15
	60	524		667		773	

It will be noted that the reaction rate is initially high in certain of the experiments. The indication is that for this initial high rate to appear, a certain minimum initial pressure is required, this pressure being the lower the higher the temperature. Thus at 400° it is between 750 and 900 mm., at 450° it is between 590 and 800 mm., at 500° it is less than 580 mm. A far more pronounced minimum pressure effect has been observed in the oxidation of phosphorus vapor by Semenoff.[7] In the latter case there is no reaction whatever below a given low pressure but instantaneous reaction above, and temperature changes do not affect the results. This behavior was attributed to the occurrence of a chain reaction. The data on ethylene may perhaps indicate a residual influence of this same nature.

Further evidence of the influence of pressure may be seen in the results of flow experiments in which ethylene was diluted with nitrogen. These will be found in Table IV. These experiments—at 575°—would have indicated that the reaction was roughly bimolecular.

There is no question but that the kinetics of the ethylene condensation are out of the ordinary. It is probable that molecular excitation and chain reaction play important roles, but the precise nature of the reaction is not clear. Combustion data indicate that the change

$$2C_2H_4 \longrightarrow C_4H_8$$

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[7] Semenoff, *Z. Physik,* 46,109 (1927).

is mildly exothermic, evolving about 17,000 cal. This, plus the original energy of activation, is to be regarded as the source of the excitation energy.

It appears that two molecules of ethylene may combine to give an excited molecule of butylene. This may subsequently become de-activated without any other effect; or it may excite a fresh ethylene molecule under favorable conditions of pressure and temperature; or, finally, it may react with a fresh ethylene molecule, producing ethane and a residue which subsequently appears in the liquid product. A more complete interpretation of the reaction must await further investigation.

Ethylene–Hydrogen.—Ethylene and hydrogen combine to form ethane in the neighborhood of 600°, the reaction being reversible but nearly complete at this temperature.[8] The reaction is of especial interest in connection with the ethylene condensation already discussed because the two must compete in some manner. Flow experiments were carried

TABLE IV

BEHAVIOR OF ETHYLENE–HYDROGEN–NITROGEN MIXTURES AT 550, 575 AND 600°

Reaction tube volume 637 cc.; total gas flow rate, 40 cc./min.

Temp., °C.	Gas in, cc.			Reacted, cc.		Formed, cc.		
	C_2H_4	H_2	N_2	C_2H_4	H_2	C_2H_6	CH_4	"C_nH_{2n}"
				50% Ethylene–Nitrogen				
550	50	0	50	5	..	2	0	2
575	50	0	50	8	..	3	0	2
600	50	0	50	11	..	5	2	4
				50% Ethylene–Hydrogen				
550	50	50	0	10	9	7	0	2
575	50	50	0	14	11	11	0	2
600	50	50	0	21	16	14	4	1
				100% Ethylene				
550	100	0	0	17	..	4	1	6
575	100	0	0	23	..	6	2	7
600	100	0	0	34	..	5	9	7
				Ethylene–Nitrogen				
575	25	0	75	2	..	0	1	1
575	50	0	50	8	..	0	3	2
575	75	0	25	13	..	0	3	4
575	100	0	0	23	..	2	6	7
				Ethylene–Hydrogen				
575	25	0	75	2	..	0	1	1
575	25	25	50	6	3	4	0	0
575	25	50	25	10	8	9	1	0
575	25	75	0	17	15	15	1	0

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[8] Pease and Durgan, THIS JOURNAL, 50,2715 (1928).

out at 550, 575 and 600° to determine the nature of the result of this competition. Data are given in Table IV.

The first three sections of Table IV give results for a 50% ethylene–nitrogen mixture, for a 50% ethylene–hydrogen mixture and for pure ethylene, each at 1 atm. and at 550, 575 and 600°. An inspection of these results makes it quite clear that hydrogenation does not occur independent of condensation. It is true that twice as much ethylene reacts in the presence of hydrogen as in the presence of nitrogen, but in the former case nearly the whole of the ethylene is hydrogenated and not merely the excess over that reacting in presence of nitrogen. Further, the product is definitely ethane and not butane, as might have been the case had butylene first been formed and then immediately hydrogenated. Again, it will be noted that the temperature coefficient of reaction rate is the same for ethylene diluted with nitrogen and for ethylene diluted with hydrogen. Finally, it may be pointed out that the sum of the ethylene and hydrogen reacting in the 50% mixture is nearly equal to the total of ethylene reacting when this substance is taken alone at 1 atm. The numbers are 19, 25 and 37 cc. for ethylene plus hydrogen, and 17, 23 and 34 cc. for ethylene alone at the three temperatures. Given half an atmosphere of ethylene, it makes little difference so far as total rate is concerned whether one adds half an atmosphere of ethylene or of hydrogen. Actually it does make some difference, hydrogen being more effective than ethylene. Thus, if we start with $^1/_4$ atm. of ethylene diluted with $^3/_4$ atm. of nitrogen, and add ethylene in one case and hydrogen on the other, we obtain the results given in the fourth and fifth sections of Table IV. The total gas reacting in a mixture of $25C_2H_4$–$75H_2$ is nearly half again as great as in pure ethylene. For total pressures of $^1/_2$, $^3/_4$ and 1 atm. at 575°, the figures for ethylene alone are 8, 13 and 23 cc. For ethylene–hydrogen mixtures they are 9, 18 and 32 cc. In the latter case, with constant ethylene concentration, the rate increases much more rapidly than the hydrogen concentration. Taking everything into consideration, it would appear that the hydrogen activates the ethylene for subsequent reaction with itself (hydrogen). Similar evidence as to the hydrogenation reaction is to be found in the work of Frey and Smith.[4]

In introducing this section of the investigation it was suggested that the hydrogenation and condensation reactions must compete. This appears to be true in the sense that the two compete for active ethylene. In absence of hydrogen this forms butylene and the other products of the condensation reaction. In presence of hydrogen it forms chiefly ethane. In addition it is not improbable that hydrogen is capable of accelerating the production of active ethylene.

It is evident that experiments at higher pressures should yield significant data regarding these reactions. It is planned to carry these out shortly.

Summary

The non-catalytic polymerization and hydrogenation of ethylene has been studied, the former between 450 and 600° and the latter between 550 and 600°. The polymerization reaction probably first produces butylene. It gives evidence of being of the chain type, and is certainly not conventional in its mechanism. The hydrogenation reaction appears to be closely coupled with the polymerization. Its rate is of the same order. Ethylene which would have polymerized is largely converted to ethane in presence of hydrogen.

PRINCETON, NEW JERSEY

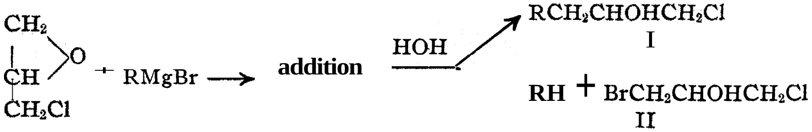
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE REACTION OF VARIOUS GRIGNARD REAGENTS WITH EPICHLOROHYDRIN. THE PREPARATION OF SOME NEW CHLOROHYDRINS

BY C. FREDERICK KOELSCH AND S. M. McELVAIN

RECEIVED OCTOBER 28, 1929 PUBLISHED MARCH 6, 1930

The reaction between epichlorohydrin and various Grignard reagents has been studied by Fourneau and Tiffeneau.[1] These investigators reported that they were unable to isolate any product formed by the development of a new carbon to carbon linkage when Grignard reagents derived from ethyl, propyl, butyl or amyl bromides were allowed to react with epichlorohydrin; in all cases the sole products obtained were the hydrocarbons formed by the hydrolysis of the Grignard reagent used, and glycerol chlorobromohydrin. However, when phenyl-, benzyl- or *p*-anisylmagnesium bromide was allowed to react with epichlorohydrin, they found that an appreciable yield of a chlorohydrin with a structure (I) could be isolated along with the hydrocarbon and glycerol chlorobromohydrin (II). These reactions may be indicated thus



In a previous paper[2] from this Laboratory it was shown that it was possible to isolate a chlorohydrin with the structure of I from the reaction of ethylmagnesium bromide and epichlorohydrin. Since this result was so different from that obtained by Fourneau and Tiffeneau, it seemed advisable to extend the study of the reaction to some of the higher alkyl

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[1] Fourneau and Tiffeneau, *Bull. soc. chim.*, [4] 1,1227 (1907).

[2] Koelsch and McElvain, THIS JOURNAL, 51, 3390 (1929).

groups and to ascertain, if possible, the effect of the structure of the group upon the course of the reaction.

This paper is a report of the results obtained by the reaction of epichlorohydrin with Grignard reagents prepared from sixteen different organic halides. The halide, the amount of epichlorohydrin used and the yields of the chlorohydrins (based on the amount of epichlorohydrin used) that were isolated are summarized in Table I. The numbers preceding each halide are used in the subsequent tables and discussion to designate the corresponding chlorohydrin or its derivative.

TABLE I

REAGENTS, QUANTITIES AND YIELDS

	RX	Amount" of epichloro-hydrin used, g.	Yield of chlorohydrin g.	%		RX	Amount" of epichloro-hydrin used, g.	Yield of chlorohydrin g.	%
1	$C_2H_5Br^b$	92.5	23.0	19	9	$(C_2H_5)_2CHCl$	29.4	5.7	10.9
2	*n*-$C_3H_7I^c$	44	2.5^d	3.9^d	10	$C_6H_{11}Cl^e$	40.6	11.9	15.3
3	*iso*-$C_3H_7I^c$	32.5	0	0	11	$C_6H_{11}CH_2Cl^e$	24.0	14.7	29.9
4	*iso*-C_3H_7Br	42.0	0	0	12	$C_6H_{10}(CH_3)Cl$ (11	5.7	0	0
5	*n*-C_4H_9Cl	46.2	12.0	16.0	13	C_6H_5Br	25.9	8.7	18.2
6	*sec.*-C_4H_9Cl	38.8	3.8	9.0	14	$C_6H_5CH_2Cl$	31.0	19.7'	32.0
7	*tert.*-C_4H_9Cl	23.0	0	0	15	$C_6H_5(CH_2)_2Cl$	28.0	7.9	12.8
8	*n*-$C_5H_{11}Cl$	39.8	21.0	29.8	16	$C_6H_5(CH_2)_3Cl$	20.0	11.5	25.0

[a] The amount of epichlorohydrin used was equivalent to the amount of RMgX actually present after the reaction of RX and Mg. [b] Koelsch and McElvain, Ref. 2. [c] The iodide was used in order that chloro-iodohydrin be formed, the higher boiling point of which permitted a better separation of the chlorohydrin by fractional distillation. The latter compound boils too near to the dichlorohydrin and the chlorobromohydrin for satisfactory fractionation. The chlorides were used in the other cases because the chlorohydrins formed have higher boiling points than glycerol dichlorohydrin, and as the size of R increases the greater the difference in the boiling points becomes. [d] This chlorohydrin was not quite pure. It was analyzed as the 3,5-dinitrobenzoate. [e] Cyclohexyl. [f] 7.8 g. of a tarry residue, not volatile at 5 mm.,[3] which was not further investigated, was left after the distillation of this chlorohydrin.

The structures of the chlorohydrins formed have been definitely established in a few cases. The chlorohydrin resulting from the action of ethylmagnesium bromide on epichlorohydrin has been shown[2] to have a structure corresponding to I. Fourneau and Tiffeneau[1] showed that phenylmagnesium bromide and *p*-anisylmagnesium bromide produced chlorohydrins with the structure of I. The chlorohydrin resulting from the action of n-butylmagnesium chloride on epichlorohydrin has the same boiling point as 1-chloroheptanol-2 which has been prepared[4] by an entirely different reaction. 1-Chloro-3-cyclohexylpropanol-2 was prepared

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[3] This fact indicates that the residue was not 1,5-diphenylpentanol-3; *cf.* Borsche and Wollemann, ***Ber.***, 45, 3721 (1912).

[4] V. Braun and Schirmacher, *ibid.*, 563,1847 (1923).

by the addition of hypochlorous acid[5] to 3-cyclohexylpropene-1. This chlorohydrin was found to be identical with the one obtained by the action of cyclohexylmagnesium chloride on epichlorohydrin.

In these representative cases it is seen that the new carbon to carbon linkage is established on the primary carbon atom of epichlorohydrin to produce a chlorohydrin with the structure of I. For this reason it was assumed that other chlorohydrins had this structure rather than the isomeric structure, $ClCH_2CHRCH_2OH$.

Experimental

Preparation of the Alkyl Halides.—The iodides were prepared from the alcohols with phosphorus and iodine. The other halides were prepared by the action of the halogen acids on the corresponding alcohols, except in the case of cyclohexylchloromethane. This halide was prepared by the action of thionyl chloride on cyclohexylcarbinol in the presence of diethylaniline. The physical properties of 3-chloropentane and cyclohexylchloromethane differed materially from those reported in the literature for these compounds. Wagner and Saytzeff[6] prepared 3-chloropentane by the action of phosphorus pentachloride on diethylcarbinol. They report the following constants for this halide: b. p. 103–105° (759 mm.); d_0 0.916; d_{21} 0.895. These values appear in the "International Critical Tables." The constants found for this compound in the present work are: b. p. 96–97° (729 mm.); d_{25}^{25} 0.8724; n_D^{25} 1.4073; M_D calcd. 30.064; found, 30.057. Gutt[7] prepared cyclohexylchloromethane from cyclohexylcarbinol and phosphorus pentachloride and reported the following constants: b. p. 98–99° (100 mm.); d_4^{22} 0.9637; n_D^{22} 1.4565; M_D calcd., 37.17; found, 37.41. The 3-chloro-pentane prepared in the present work has the following constants: b. p. 67–68° (20 mm.); d_{25}^{25} 0.9815; n_D^{25} 1.4630; M_D, calcd., 37.168; found, 37.179.

Preparation of the Chlorohydrins.—To 0.25–0.5 atom of magnesium turnings covered with 100–200 cc. of ether was added a few cc. of a solution of an equivalent amount of the halide in twice its volume of ether. A small crystal of iodine was added and the reaction was started by heating. The remainder of the halide solution was added slowly with stirring and the mixture then refluxed for half an hour on a water-bath. The solution of the Grignard reagent was cooled and transferred to a long, graduated, cylindrical dropping funnel, where its volume was measured. Two cc. of the solution was pipetted out and added to 5 cc. of 1.0 N hydrochloric acid dissolved in 20 cc. of water. The solution was warmed to dissolve the magnesium hydroxide and to remove the ether, and the excess acid was titrated with $N/10$ sodium hydroxide solution.[8] In the preparation of the Grignard reagents from the tertiary alkyl halides, the quantity of ether used was twice that given above, and the magnesium chloride etherate formed as a by-product in the preparation of the Grignard reagent was removed by centrifuging and decanting the supernatant liquid.

The Grignard reagent was added from the dropping funnel to a solution of an equivalent amount of epichlorohydrin in an equal volume of ether, the rate of addition being

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[5] Michael has shown [*J. prakt.* Chem., [2] 64, 105 (1901)] that in the addition of hypochlorous acid to an unsymmetrical olefin, the hydroxyl group of the hypochlorous acid becomes attached to the carbon atom poorer in hydrogen. This generalization is in accord with the fact that the two chlorohydrins mentioned above are identical.

[6] Wagner and Saytzeff, ***Ann.,*** 179, 321 (1875).

[7] Gutt, Ber., 40, 2067 (1907).

[8] *Cf.* Gilman and others, **THIS JOURNAL,** 45, 153 (1923).

regulated so that the mixture refluxed gently. After the addition was completed, the refluxing was continued on a water-bath for one hour; finally the mixture was allowed to stand at room temperature for twenty-four hours. The mixture was then hydrolyzed with ice and dilute sulfuric acid and the ether layer separated. The ether solution was washed with dilute sodium carbonate solution and finally with water. The ether was distilled off through a fractionating column, and the residue was fractionally distilled under diminished pressure. The product was separated by repeated fractional distillation into: (a) the chlorohydrin, (b) glycerol dichlorohydrin (or the corresponding bromo- or iodo- compound), and in some cases (c) the hydrocarbon formed by the hydrolysis of the Grignard reagent. Fractions (b) and (c) were identified by boiling points and densities. The yields of the chlorohydrins (fraction a) are shown in Table I and the physical constants and analyses in Table II.

TABLE II

PHYSICAL CONSTANTS AND ANALYSES OF THE CHLOROHYDRINS

No.	Chlorohydrin	Boiling point, uncorrected °C.	Mm.
2	1-Chlorohexanol-2	72–74	12
5	1-Chloroheptanol-2	92–94	13
6	1-Chloro-4-methylhexanol-2	82–84	13
8	1-Chloro-octanol-2	104–107	13
9	1-Chloro-4-ethylhexanol-2	103–104	15
10	1-Chloro-3-cyclohexylpropanol-2	122–124	11
11	1-Chloro-4-cyclohexylbutanol-2	142–144	12
13	1-Chloro-3-phenylpropanol-2	142–144	23
14	1-Chloro-4-phenylbutanol-2	158–160	23
15	1-Chloro-5-phenylpentanol-2	152–154	8
16	1-Chloro-6-phenylhexanol-2	147–148	2.5

No.	Formula	d_{25}^{25}	n_D^{25}	M_D Calcd.	M_D Pound	Chlorine (Carius), % Calcd.	Chlorine (Carius), % Found
5	$C_7H_{15}OCl$	0.9931	1.4474	40.79	40.73	23.6	23.9
6	$C_7H_{15}OCl$	0.9915	1.4503	40.79	40.83	23.6	23.5
8	$C_8H_{17}OCl$	0.9715	1.4485	45.39	45.36	21.6	21.2
9	$C_8H_{17}OCl$	0.9828	1.4528	45.39	45.23	21.6	21.4
10	$C_9H_{17}OCl$	1.0533	1.4854	47.89	48.06	20.1	20.1
11	$C_{10}H_{19}OCl$	1.0305	1.4832	52.50	52.70	18.6	18.0
13	$C_9H_{11}OCl$	1.1528	1.5470	46.71	46.90	20.8	20.0
14	$C_{10}H_{13}OCl$	1.1203	1.5375	51.41	51.48	19.2	19.3
15	$C_{11}H_{15}OCl$	1.0895	1.5320	56.17	56.45	17.9	17.9
16	$C_{12}H_{17}OCl$	1.0710	1.5262	60.77	60.78	16.6	16.2

Preparation of the 3,5-Dinitrobenzoates.—These esters were obtained practically quantitatively by the following procedure. To a mixture of 1.0 g. of the chlorohydrin with 0.8 of the theoretical amount of 3,5-dinitrobenzoyl chloride was added 5 cc. of dry pyridine. The mixture was stoppered and shaken, and allowed to stand overnight. Water was then added and the separated oil taken up in ether. The ethereal solution was washed with dilute hydrochloric acid, water, dilute sodium carbonate solution and finally again with water. The ether was evaporated off and the residual ester was crystallized from alcohol until its melting point was not changed by further crystallization. The melting points and analyses of these esters are given in Table III.

3-Cyclohexylpropylene-1,2-oxide.—It seemed that the structure of the chlorohydrin derived from cyclohexylmagnesium chloride and epichlorohydrin might be

TABLE III

ANALYSES AND MELTING POINTS OF THE 3,5-DINITROBENZOATES OF THE CHLOROHYDRINS

No.[a]	M. p., °C. (uncorr.)	Formula	Chlorine (Carius), % Calcd.	Found
2	65–66	$C_{13}H_{15}O_6N_2Cl$	11.0	10.7
5	59	$C_{14}H_{17}O_6N_2Cl$	10.3	10.5
6	49–50	$C_{14}H_{17}O_6N_2Cl$	10.3	10.3
8	55	$C_{15}H_{19}O_6N_2Cl$	9.9	10.0
9	Oil	$C_{15}H_{19}O_6N_2Cl$	...	...
10	95–96	$C_{16}H_{19}O_6N_2Cl$	9.59	9.58
11	107–108	$C_{17}H_{21}O_6N_2Cl$	9.23	9.32
13	120–121	$C_{16}H_{18}O_6N_2Cl$	9.75	9.72
14	Oil	$C_{17}H_{15}O_6N_2Cl$	...	...
15	106–107	$C_{18}H_{17}O_6N_2Cl$	9.04	9.01
16	Oil	$C_{19}H_{19}O_6N_2Cl$	...	...

[a] The numbers in this column indicate the 3,5-dinitrobenzoates of the correspondingly numbered chlorohydrins of Table II.

definitely established by converting it into 3-cyclohexylpropylene-1.2-oxide which has been described by Rességuier.[9] Accordingly a solution of 8.87 g. (0.05 mole) of the chlorohydrin in dry ether was treated with 2.2 g. (0.057 mole) of finely powdered sodium hydroxide. The flask was stoppered tightly and shaken intermittently for four hours. The mixture was then allowed to stand for twelve hours at room temperature, after which it was refluxed for thirty minutes. The reaction mixture was then cooled and filtered and the solid residue washed with three 10-cc. portions of dry ether After removal of the ether the remaining oxide was distilled. The distillate weighed 3.69 g. and boiled at 197–200° (740 mm); d_{25}^{25} 0.9357, n_D^{25} 1.4572; M_D, calcd., 41.008; found, 40.859.

Anal. Subs., 0.2707: CO_2, 0.7670; H_2O, 0.2792. Calcd. for $C_9H_{16}O$: C, 77.13; H, 11.43. Found: C, 77.25; H, 11.51.

Rességuier reports the following constants for this oxide: b. p. 182–185°; d_0 1.003. Since the constants of the oxide as found in the present work differ so markedly from those of Rességuier, and since the chlorohydrin from which the oxide was derived is shown below to be 1-chloro-3-cyclohexylpropanol-2, it is necessary to conclude that Rességuier's oxide was quite impure.

1-Chloro-3-cyclohexylpropanol-2 from 3-Cyclohexylpropene-1.—Since it was not possible to establish the structure of the chlorohydrin by comparing the oxide derived from it with Rességuier's 3-cyclohexylpropylene-1,2-oxide, it was necessary to prepare 1-chloro-3-cyclohexylpropanol-2. This was accomplished in the following manner. A solution of hypochlorous acid was prepared according to the directions of Wohl.[10] To 500 cc. of this solution (titrating 1.9% HOCl) was added 22 g. of 3-cyclohexylpropene-1 (prepared from allyl bromide and cyclohexylmagnesium chloride), the temperature being kept at about 10° during the addition. The mixture was stirred for two hours and allowed to stand at room temperature overnight. The heavy oil was separated. The aqueous portion of the reaction mixture was extracted twice with 50-cc. portions of ether and the oil obtained from these extracts after evaporating off the ether was added to the main portion. The oil was washed with a little sodium bisulfite solution and finally with a little water. It was then distilled at 13 mm. and the following fractions collected: 118–123° (8.8 g.); 123–133° (3.3 g.); residue, not volatile without decom-

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[9] Rességuier, *Bull. soc. chim.*, [4] 15, 175 (1914).

[10] Wohl, *Ber.*, 40, 94 (1907).

position (14.5 g.). One gram of the fraction boiling at 118–123° was converted into the 3,5-dinitrobenzoate, which melted at 95–96°. The melting point of a mixture of this 3,5-dinitrobenzoate with the 3,5-dinitrobenzoate of the chlorohydrin prepared from epichlorohydrin and cyclohexylmagnesium chloride was 95–96°. This comparison leaves no doubt as to the structure of the latter compound.

Oxidation of 1-Chloro-4-phenylbutanol-2 to Benzoic Acid.—In view of the frequent formation of o-tolyl compounds from benzylmagnesium chloride and carbonyl compounds,[11] it seemed advisable to determine whether the chlorohydrin resulting from the action of benzylmagnesium chloride on epichlorohydrin contained the phenyl or the tolyl radical. This was done by oxidizing the chlorohydrin with potassium permanganate to benzoic acid, which was identified by its melting point and neutral equivalent.

Discussion of Results

The yield of chlorohydrin obtained by the reaction of epichlorohydrin with an alkylmagnesium halide seems to depend on the structure and on the molecular weight of the latter. The Grignard reagents derived from the primary alkyl halides gave much higher yields than those derived from secondary alkyl halides, while those from the tertiary alkyl halides gave such small yields of chlorohydrins (if any at all) that these compounds could not be isolated from the reaction mixtures. Apparently the nature of the halogen is not without effect on the yield. Although no particular study was made of this effect, the reaction of *n*-propylmagnesium iodide with epichlorohydrin to give a yield of only 3.9% indicates that the alkylmagnesium iodides give a smaller yield of chlorohydrin than do the chlorides or bromides. It was also noted that as the weight of the alkyl radical became greater, the yield of chlorohydrin was raised (cf. Nos. 5, 8, 11; Nos. 4, 6, 9 and 10, Table I). The introduction of an aromatic group into the Grignard reagent caused the yield in some cases to rise above, and in others to fall below, that which would be expected from a Grignard reagent containing an alkyl group of an equal size. There appears to be a certain periodicity in the yield of chlorohydrin from these phenyl-substituted Grignard reagents (Nos. 13, 14, 15 and 16, Table I) but the data at hand are hardly sufficient to warrant any definite conclusions on this point.

Summary

1. The reaction between epichlorohydrin and sixteen different Grignard reagents has been studied. It has been shown that 1,2-chlorohydrins are formed when the Grignard reagents are derived from primary and secondary (except isopropyl) alkyl halides.

2. The effect of the structure of the Grignard reagent on the course of the reaction is discussed.

MADISON, WISCONSIN

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[11] Gilman and Harris, THIS JOURNAL, 49, 1825 (1927).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE PREPARATION OF 5-BROMOFURFURAL AND SOME OF ITS DERIVATIVES

BY HENRY GILMAN AND GEORGE F. WRIGHT

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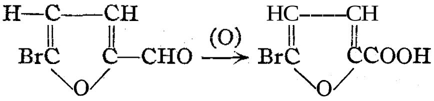
Introduction

One of the outstanding characteristics of aromatic compounds is the smooth and readily controlled substitution reactions which they undergo. Some heterocyclic types like furan, thiophene and pyrrole have physical, chemical and physiological properties which warrant their correlation with an aromatic compound like benzene.[1] For these reasons it is somewhat surprising that no bromofurfural is described in the literature, particularly because most of the reactions of furan have centered about the readily accessible and inexpensive furfural. Undoubtedly a chief reason for the difficulty in the preparation of bromofuran compounds is the great sensitiveness of the furan ring to halogens and halogen acids.

We have shown that it is possible to prepare 5-bromofurfural in relatively satisfactory yields by the direct bromination of furfural diacetate, the synthesis of which has been improved by recent directions of Gilman and Wright.[2] The position of the bromine atom in our bromofurfural was established by its oxidation to the known 5-bromofurfuroic acid.



There were prepared from 5-bromofurfural, in addition to the 5-bromofuroic acid, the oxime and diacetate.

Experimental Part

Several experiments, with variations, were carried out for the synthesis of 5-bromofurfural.

First, 198 g. (1.0 mole) of furfural diacetate, prepared in accordance with the directions of Gilman and Wright,[2] was dissolved in 400 cc. of carbon disulfide which had been dried by shaking with anhydrous calcium chloride. To this stirred solution contained in a one-liter, three-necked flask provided with a mechanical stirrer, condenser and separatory funnel, was added 320 g. (2 moles) of bromine.[3] The addition of bromine was effected in about a one-hour period and at room temperature. After refluxing over a water-bath for ten hours, the mixture was poured upon 100 g. of precipitated calcium carbonate contained in a two-liter steam distillation flask, and there allowed to react for about fifteen minutes. Then 125 cc. of water was added and steam was admitted

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[1] Gilman and Pickens, THIS JOURNAL, 47, 245 (1925).

[2] Gilman and Wright, *Iowa State College J. of Science, 4,* **35** (1929).

[3] The bromine was first dried by shaking with concentrated sulfuric acid and then distilled.

very *slowly* and *cautiously*. When the carbon disulfide had distilled over, the temperature of the condenser was raised to about 60–80° (by regulating the flow of cooling water), and the condensate was collected in a flask well cooled by water. The white solid obtained in this manner was redistilled with steam and yielded 41.5 g. or 23.7% of the theoretical amount of 5-bromofurfural which melted at 81.5–82°. When the quantity of bromine is increased under these conditions to 352 g. or 2.2 moles, the yield of bromofurfural is decreased considerably, and there also results, in a 4–5% yield, an as yet unidentified compound which melts at 134–135° when purified by steam distillation. This compound contains two atoms of bromine and gives a positive test with Tollens' reagent.

In a second preparation starting with 0.25 mole of furfural diacetate the bromine was added over a two-hour period during which the reaction mixture was kept at 10°. After stirring at this temperature for four hours, it was chilled to −15° and filtered. The filtrate was distilled under reduced pressure until most of the solvent was removed, and then the residue was carefully steam distilled to yield 12 g. or 27.3% of the bromofurfural melting at 81.5–82°. This method is, at present, preferred to the others.

Third, 49.5 g. (0.25 mole) of furfural diacetate in 100 cc. of chloroform was added to a chilled solution of a pyridine-bromine complex, prepared by adding 80 g. (0.5 mole) of bromine to 39.5 g. (0.5 mole) of pyridine in 100 cc. of carbon disulfide, to which was then added 100 cc. of chloroform. After allowing this mixture to stand for three days with occasional shaking, it was extracted with water and dilute acetic acid, and dried with anhydrous sodium sulfate. It was first distilled at 90–95° (8 mm.) and melted at 80°. Then on steam distillation, 15 g., or 34.1%, of the bromofurfural was obtained and this melted at 82°. Bromofurfural appears to be more stable than furfural, a not entirely unexpected phenomenon.

Anal. Calcd. for $C_5H_3O_2Br$: Br, 45.45. Found: Br, 45.97, 45.97.

In other experiments it was found that lower yields of the bromofurfural were obtained with smaller molecular proportions of bromine. The use of acetic anhydride as a solvent[4] at a temperature below 0°, also gave a lower yield of bromofurfural. With acetic anhydride as the solvent, some acetyl bromide and a smaller quantity of bromoacetyl bromide were detected.

Oxidation of **5-Bromofurfural.**—The oxidation was effected in a 34% yield by adding aqueous potassium permanganate to 17.6 g. (0.1 mole) of bromofurfural suspended in water containing calcium hydroxide. The identity of the 5-bromofuroic acid was confirmed by a mixed melting point determination with the acid prepared in accordance with the method of Hill and Sanger.[5]

5-Bromofurfuraldoxime, $BrC_4H_2OCH{=}NOH$.—The oxime was prepared in the usual manner from the aldehyde, hydroxylamine hydrochloride and 10% sodium hydroxide. The yield (from 5 g. of the bromofurfural) was 75%. The oxime melts at 150–152°, and has a pleasant sweet taste.[6]

Anal. Calcd. for $C_5H_4O_2NBr$: Br, 42.10. Found: Br, 42.62.

5-Bromofurfural Diacetate, $BrC_4H_2OCH(OCOCH_3)_2$.—Forty-four g. (0.25 mole) of bromofurfural was refluxed for ten hours with 83.6 g. (0.82 mole) of acetic anhydride

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[4] The acetic anhydride was used to stabilize the diacetate, a procedure now employed in this Laboratory for other substitution reactions of furan compounds. The diacetate is more conveniently and less expensively prepared than the diacetal of furfural.

[5] Hill and Sanger, *Ann.*, **232**, 46 (1885).

[6] See Gilman and Hewlett, *Iowa State College J. of Science*, 4, 27 (1929), for a recent article on the correlation of sweet taste with constitution of some furan compounds.

and 9.6 g. (0.16 mole) of acetic acid. Distillation under reduced pressure yielded a low-boiling fraction, and a higher fraction distilling at 148–150" (11 mm.). The low-boiling fraction was refluxed for six hours with 75.5 *g*. (0.75 mole) of acetic anhydride and the mixture, after standing for several days, was distilled in a vacuum as before. The total yield of diacetate distilling at 128–130° (5–6 mm.) and melting at 51–52' was 60 g. or 87%. Hydrolysis with normal sulfuric acid gave 5-bromofurfural.

Anal. Calcd. for $C_9H_9O_5Br$: Rr, 28.88. Found: Br, 29 02, 29.00.

Summary

The first bromofurfural, 5-bromofurfural, has been prepared by the direct bromination of furfural diacetate and characterized by a few appropriate derivatives.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY OF THE UNIVERSITY OF MARYLAND SCHOOL OF MEDICINE]

THE PHENYLATION OF OLEIC ACID

BY E. G. SCHMIDT

RECEIVED OCTOBER 28, 1929 PUBLISHED MARCH 6, 1930

As a preliminary step in the study of the metabolism of certain fatty acids the introduction of various aromatic groups into the double bond of oleic acid has been investigated. Eijkman[1] as well as Marcusson[2] have studied the reaction between unsaturated fatty acids, benzene and anhydrous aluminum chloride with the production of phenyl-substituted saturated acids; however, if the double bond was in the α-position to the carboxyl group, phenylation did not take place. Marcusson drew attention to the fact that Poncio and Castaldi[3] found that these same acids had no iodine number and he pointed out the parallelism between unsaturated fatty acids which do not absorb iodine from Hubl's solution and non-reactivity with aromatic compounds in the presence of aluminum chloride. Nicolet and deMilt[4] noted that the derivatives of phenylstearic acid show little tendency to crystallize.

In the present work the reaction between benzene and oleic acid in the presence of anhydrous aluminum chloride has been studied with particular reference to the speed of the reaction and to the length of the reaction period as affecting the nature of the condensation products. The reaction proceeded with great speed and with a vigorous evolution of hydrogen chloride, and within less than five minutes it was practically completed, as determined by the drop in the iodine number and the neutralization equivalent. If the reaction was allowed to proceed for several hours, par-

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[1] Eijkman, ***Chem. Centr.*, II,** 1100 (1908).

[2] Marcusson, Z. ***angew. Chem.*, *33*,** 231 (1920).

[3] Poncio and Castaldi, ***Chem. Centr.*, II,** 1154 (1912).

[4] Nicolet and deMilt, THIS JOURNAL, 49, 1103 (1927).

ticularly in the presence of an excess of aluminum chloride, a dark product with a neutralization equivalent much less than that required for phenylstearic acid was obtained. A similar effect was produced by the use of a considerable excess of aluminum chloride. The reaction went on best in the presence of approximately equimolecular quantities of oleic acid and aluminum chloride; with less than one-third of the equivalent quantity of aluminum chloride, very little condensation seemed to take place.

Experimental

Experiment 1.—The Phenylation **of** Oleic Acid.—In the first experiment 40 g. of oleic acid was dissolved in 225 cc. of benzene to which was added 28 g. of aluminum chloride during the course of about five minutes. Upon the introduction of the aluminum chloride there immediately resulted a vigorous evolution of heat and hydrogen chloride. After refluxing for about thirty minutes, the product was cooled, dissolved in 400 cc. of ether and gently mixed with 200 cc. of 20% hydrochloric acid. The aqueous layer was removed and the reaction product was shaken with water until free from hydrochloric acid. The solution was distilled from the water-bath and the final traces of solvents were removed from the oily residue by distillation from the water-bath, under reduced pressure. The final product was a light brown oil similar to oleic acid and was used without further attempts at purification. It had an iodine number of 10, a neutralization equivalent of 160.4 and the analysis of the silver salt gave the following data.

Anal. Subs., 0.6004: Ag, 0.1381. Calcd. for $C_{24}H_{39}O_2Ag$: Ag, 23.1. Found: Ag, 23.0.

Experiment 2.—In the next series of experiments the effect of varying the amount of aluminum chloride and the time the mixture was refluxed was studied. The data are given in Table I and indicate that the reaction would not proceed unless a considerable quantity of aluminum chloride was present but an excess produced compounds of lower neutralization equivalent, and a similar effect was produced if the reaction mixture was boiled too long. Complete saturation was never obtained.

TABLE I

THE EFFECT OF VARYING THE AMOUNT OF ALUMINUM CHLORIDE

Oleic acid, g	Benzene, cc.	$AlCl_3$, g	Refluxed, hrs	Iodine, no.	Neut. equiv.[a]
40	225	0	0	91.0	197
40	225	7	1	89.7	193
40	225	7	3	88.7	193
40	225	14	1	33.3	176
40	225	14	3	32.4	173
40	225	21	1	14.6	158
40	225	21	3	11.1	157
40	225	28	1	10.0	159
40	225	28	3	7.1	158
40	225	40	3	15.0	122
40	225	65	1	12.0	129
40	225	65	3	11.1	105

[a] Calcd. for phenylstearic acid, 156.6.

Experiment **3.—In** this experiment the speed with which phenylation took place and the effect of prolonged heating upon the final product were studied. Sixty grams of oleic acid was dissolved in 300 cc. of benzene and a 25-cc. aliquot was removed for analysis; 35 g. of aluminum chloride was added rapidly with shaking and after three minutes 25 cc. was removed, immediately dissolved in ether and treated with dilute hydrochloric acid to stop the reaction. In the meantime the reaction mixture was refluxed on the water-bath and at various intervals an aliquot was removed and worked up as outlined in the first experiment. The data are given in Table II and indicate that phenylation is extremely rapid—within three minutes the reaction had practically reached completion. If the mixture was allowed to boil too long, a product with a low neutralization equivalent was obtained.

TABLE II

THE EFFECT OF THE LENGTH OF THE REACTION PERIOD

Refluxed, min.	0	3	7	11	30	60	120	180	240
Iodine number	90.8	9.7	11.0	12.1	10.0	13.0	11.5	9.0	13.6
Neut. equiv.[a]	197.0	161.4	160.5	161.0	160.6	159.3	156.0	140.3	133.0

[a] Calcd. for phenylstearic acid, 156.6.

Experiment 4.—The reaction of oleic acid with xylene was studied in a similar manner and was found to proceed with equal rapidity, yielding an oil similar in appearance and properties to phenylstearic acid. The product had an iodine number of 13 and a neutralization equivalent of 144; calcd. for xylylstearic acid, 144.1.

Anal. (silver salt). Subs., 0.5838; Ag, 0.1286. Calcd. for $C_{26}H_{43}O_2Ag$: Ag, 21.77. Found: Ag, 22.02.

Summary

Phenylation of oleic acid with the production of phenylstearic acid proceeded with great speed in the presence of approximately equimolecular quantities of aluminum chloride and oleic acid and an excess of benzene. A considerable excess of aluminum chloride or prolonged boiling of the reaction mixture produced compounds having lower neutralization equivalents than that of phenylstearic acid.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

STUDIES IN THE CYCLOPROPANE SERIES. XIII. A NEW TYPE OF CYCLOPROPENE DERIVATIVE

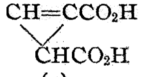
BY E. P. KOHLER AND S. F. DARLING

RECEIVED NOVEMBER 1, 1929 PUBLISHED MARCH 6, 1930

In various papers of this series we have discussed the possibility that cyclopropene derivatives might serve as intermediates in the process by which bases convert nitro cyclopropanes into open-chained compounds. The open-chained products are unsaturated and they do not contain the nitro group; but since no cyclopropene derivatives were isolated in any of these cases, the loss of nitrous acid might have occurred either before or after the opening of the ring. We decided, therefore, to determine whether a cyclopropene can actually be formed by eliminating nitrous acid from a suitably constituted nitro cyclopropane.

The choice of suitable material was based on the following consideration.

The only type of cyclopropene derivative that is known to be stable in the presence of bases is that represented by the acids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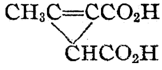
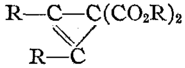
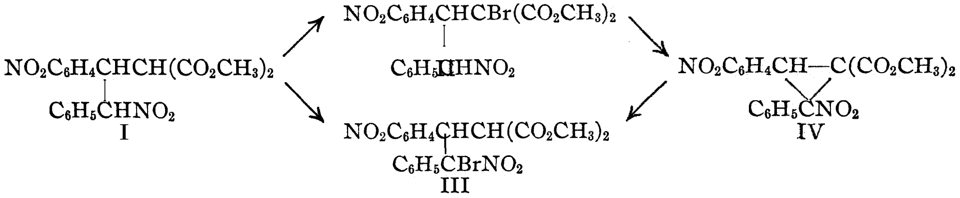

(a)

No methods are known for making nitro cyclopropanes which could form derivatives of this type by loss of nitrous acid, and none are available for making the corresponding ketones or other dicarbonyl compounds which would doubtless be equally stable, An inquiry into the reason for the stability of this type, in which all the facts that are known with respect to the preparation and properties of cyclopropene derivatives were considered, led Goss, Ingold and Thorpe[1] to the conclusion that the (a) hydrogen atom is essential for stability. Their argument appears to us to be inconclusive, because it completely ignores the significance of conjugated systems.

It seemed to us that cyclopropene derivatives that contain no conjugated system which would promote the addition of bases, and no hydrogen which by shifting could generate such a conjugated system, should be sufficiently stable to withstand even the intensive action of alkalies that is required for eliminating nitrous acid. We, therefore, decided to prepare a cyclopropene derivative of the type



For our purpose, then. it was essential to start with a nitro cyclopropane derivative which contained but one available hydrogen atom. We planned to secure such a derivative by adding phenylnitromethane to a nitro benzal malonic ester, brominating the addition product in the α- and γ-positions and eliminating hydrogen bromide from one or other of the resulting bromo compounds



The addition product was obtained without difficulty. When it was brominated directly it gave a single monobromo derivative—doubtless the α-bromo compound II because the hydrogen *a*- to a nitro group cannot be replaced by bromine in neutral or acid solutions. Elimination of hydrogen bromide from the monobromo derivative likewise gave but one product. This is not necessarily the cyclopropane derivative because this reaction

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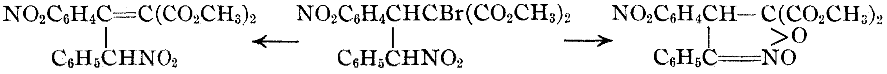
[1] Goss, Ingold and Thorpe, J. *Chem. Soc.*, **123,330** (1923).

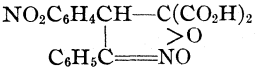
may result in the formation of an isoxazoline oxide,[2] and, since it is necessary to employ bases for eliminating hydrogen bromide, it is conceivable also that an unsaturated nitro compound might be formed as a secondary product.



$$\begin{array}{c} NO_2C_6H_4C{=}C(CO_2CH_3)_2 \\ | \\ C_6H_5CHNO_2 \end{array} \longleftarrow \begin{array}{c} NO_2C_6H_4CHCBr(CO_2CH_3)_2 \\ | \\ C_6H_5CHNO_2 \end{array} \longrightarrow \begin{array}{l} NO_2C_6H_4CH{-}C(CO_2CH_3)_2 \\ \qquad | \qquad >O \\ C_6H_5C{=}NO \end{array}$$

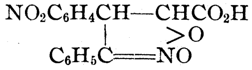
II V

Any unsaturated nitro compound that could possibly result from this reaction would be expected to form a sodium compound, to combine with ozone, and to be readily cleaved into dimethyl malonate and benzoyl phenylnitromethane. Our product undergoes none of these transformations. It was hydrolyzed to the corresponding dibasic acid and when this was boiled with water it ultimately passed into an isoxazole derivative—a behavior that is characteristic of certain isoxazoline oxides.



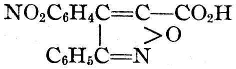
$$\begin{array}{l} NO_2C_6H_4CH{-}C(CO_2H)_2 \\ \qquad | \qquad >O \\ C_6H_5C{=}NO \end{array}$$

VI



$$\begin{array}{l} NO_2C_6H_4CH{-}CHCO_2H \\ \qquad | \qquad >O \\ C_6H_5C{=}NO \end{array}$$

VII



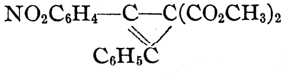
$$\begin{array}{l} NO_2C_6H_4C{=}C{-}CO_2H \\ \qquad | \qquad >O \\ C_6H_5C{=}N \end{array}$$

VIII

Since the cyclopropane derivative could not be obtained from this a-bromo compound, it was necessary to undertake the preparation of a ?-bromo compound by way of the sodium compound. The addition product has two hydrogen atoms that are replaceable by metals, but when a solution in sodium methylate was added to bromine, it yielded a single monobromo derivative which was isomeric with the substance obtained by direct bromination. Elimination of hydrogen bromide from this second bromo compound resulted in two isomers which were formed in approximately equal amounts. One of these isomers was the isoxazoline oxide V; this bromo compound, is, therefore, likewise an a-bromo derivative.

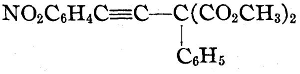
Fortunately for our project the second bromine-free product gave none of the typical reactions of isoxazoline oxides. When it was treated with sodium methylate it lost nitrous acid—a reaction that never occurs with these oxides but is characteristic of nearly all nitro cyclopropane derivatives. In this as in a few other cases, therefore, the a-bromo compound yields both oxide and cyclopropane.

Since the product obtained by eliminating nitrous acid from the cyclopropane derivative has no hydrogen atoms that are not tied up in its phenyl and ester groups, the number of its possible formulas is small

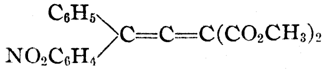


$$\begin{array}{l} NO_2C_6H_4{-}C{-}C(CO_2CH_3)_2 \\ \qquad \diagdown\!\!\diagdown\;\diagup \\ \quad C_6H_5C \end{array}$$

IX



$$\begin{array}{l} NO_2C_6H_4C{\equiv}C{-}C(CO_2CH_3)_2 \\ \qquad\qquad\qquad | \\ \qquad\qquad\quad C_6H_5 \end{array}$$



$$\begin{array}{l} C_6H_5\diagdown \\ \qquad\quad C{=}C{=}C(CO_2CH_3)_2 \\ NO_2C_6H_4\diagup \end{array}$$

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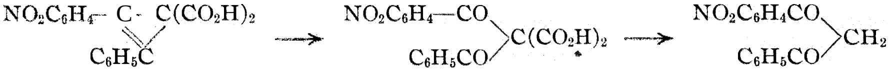
[2] Kohler and Barrett, THIS JOURNAL, 48, 1770 (1926)

In order to distinguish between these formulas we hydrolyzed the substance to the corresponding dibasic acid and then oxidized this acid with permanganate. The product was nitro dibenzoyl methane, proving conclusively that the substance is the cyclopropene derivative



X XI

The isolation of this cyclopropene derivative justifies the assumption that cyclopropene derivatives may play a role in the passage of nitro cyclopropane derivatives into open-chained compounds. It also proves that the stability of cyclopropene derivatives is not dependent on the presence of a "mobile hydrogen atom." Since it has no conjugated system, the ester is more stable even than the ester of methyl cyclopropene dicarboxylic acid; it is not attacked at all by hot concentrated sodium methylate.

Experimental Part

I. The Isoxazoline Oxide and its Degradation

The reactions that lead to the formation of the isoxazoline oxide are exactly the same as those employed by Kohler and Barrett[2] for making the corresponding compound without the m-nitro group, but owing to the influence of the nitro group in diminishing solubility, all operations are much simpler. Since the bromination of the addition product is not easy, it is necessary to use pure material for this step; in all other transformations thoroughly washed and dried crude products serve equally well.

Dimethyl β-(3-Nitrophenyl)-γ-nitro-γ-phenyl-ethylmalonate, I.—A solution of 40 g. of the methyl ester of m-nitro benzal malonic acid and 20 g. of phenylnitromethane in 200 cc. of dry methyl alcohol containing a little sodium methylate was boiled for half an hour, then diluted with 100 cc. of ether and a small quantity of water. It deposited 47 g. of addition product. The substance was purified by recrystallization from a mixture of ether and petroleum ether or from methyl alcohol. It is sparingly soluble in ether, moderately soluble in methyl alcohol, and it crystallizes in silky needles which melt at 118–120°.

In a few cases the addition product melted at a considerably lower temperature. In these cases, there were indications of the presence of an isomeric addition product that crystallized in stouter needles. Since this was, doubtless, a stereoisomer, no attempt was made to isolate it.

Anal Calcd. for $C_{19}H_{18}O_8N_2$: C, 56.7; H, 4.5. Found: C, 57.1; H, 4.5.

The a–Bromo Compound Formed by Direct Bromination, 11.—The addition product was brominated by adding excess of bromine to a solution of the substance in chloroform. In order to start the process it was necessary to expose the heated solution to direct sunlight. Once it was started it proceeded under the influence of sunlight alone but took several hours for its completion. When the evolution of hydrogen bromide ceased, the solvent was removed and the oily residue rubbed with a little methyl alcohol until it solidified. The yield of crude, washed and dried solid was 24 g. from 25 g. of substance. The bromo compound was recrystallized from methyl alcohol, from which it separated in fine colorless needles melting at 125°.

Anal. Calcd. for $C_{19}H_{17}O_8N_2Br$: C, 47.4; H, 3.5. Found: C, 47.4; H, 3.6.

Dimethyl 3-Phenyl-4-(3-nitrophenyl)-5,5-isoxazoline Oxide Dicarboxylate, V.—A suspension of 10 g. of the bromo compound and 10 g. of potassium acetate in 100 cc. of methyl alcohol was boiled until all of the bromo compound had disappeared. The light yellow solution was then cooled, the precipitate collected on a filter, washed with water and methyl alcohol and dried; yield, 7.5 g. of pure oxide. The oxide separates from methyl alcohol, in which it is sparingly soluble, in large very pale yellow monoclinic crystals. It melts at 173–174°.

Anal. Calcd. for $C_{19}H_{16}O_8N_2$: C, 57.0; H, 4.0. Found: C, 57.5; H, 4.3.

Hydrolysis to the Dibasic Acid, **VI.**—A solution of the oxide in cold methyl alcoholic potassium hydroxide is pale yellow in color but it immediately turns red on heating. A red solution like this was heated on a steam-bath for ten minutes, then diluted with a large volume of water and acidified. The precipitated acid was extracted with ether, the ethereal solution filtered, dried and allowed to evaporate. It deposited large pale yellow crystals which melted with vigorous effervescence. The effervescence is due to a molecule of ether, which cannot be completely removed without decomposing the acid, but which appears promptly when the acid is dissolved in bases. The acid will not crystallize in the absence of ether.

Anal. Calcd. for $C_{17}H_{12}O_8N_2 \cdot (C_2H_5)_2O$: C, 56.5; H, 5.0; equiv. wt., 223. Found: C, 56.6; H, 5.3; equiv. wt., 222.

In order to make certain that hydrolysis was not accompanied by rearrangement, the acid was re-esterified by digesting its dry, colorless silver salt with methyl iodide in absolute ether; it gave the original ester in the calculated quantity.

Hydrolysis and Cleavage. 3-Phenyl-4-(3-nitrophenyl)-isoxazoline Oxide Carboxylic Acid, **VII.**—Two g. of the diester was dissolved in an ice-cold solution containing 2 g. of sodium in the minimum amount of methyl alcohol. The solution turned red as its temperature rose to that of the room. After twenty-four hours at the room temperature it had become deep red in color and had deposited a small quantity of solid. It was cleared by filtration, diluted with water and acidified. The (acid) solution deposited pale yellow needles which became colorless when recrystallized from ether–petroleum ether and then melted with decomposition at about 190°.

Anal. Calcd. for $C_{16}H_{12}O_6N_2$: C, 58.6; H, 3.7; equiv. wt., 328. Found: C, 58.7; H, 4.0; equiv. wt., 323.

The monobasic acid forms a colorless silver salt and a sparingly soluble sodium salt which crystallizes in needles. It is not attacked by ozone and its solution in sodium carbonate does not reduce permanganate.

The Methyl Ester.—The dry silver salt of the monobasic oxido acid was digested with an excess of methyl iodide. The product crystallized from ether–petroleum ether in pale yellow prisms melting at 133°.

Anal. Calcd. for $C_{17}H_{14}O_6N_2$: C, 59.7; H, 4.1. Found: C, 59.9; H, 4.0.

The ester does not dissolve in cold concentrated sodium methylate and it does not form an ozonide. It is therefore neither an unsaturated nitro compound nor a cyclopropane derivative.

3-Phenyl-4-(3-nitrophenyl)-isoxazole Carboxylic Acid, **VIII.**—When the dibasic acid is heated with water it first loses ether, then dissolves. The resulting clear solution, on longer heating, turns faintly red, becomes turbid and deposits an oil that has the odor of phenylnitromethane. From an ethereal solution of this oil sodium bicarbonate extracts a relatively small quantity of the isoxazole acid. The acid was also obtained as a by-product in the formation of the isoxazoline oxide and cyclopropane esters. It crystallizes in small pale yellow rhombs and decomposes at about 300°.

Anal. Calcd. for $C_{16}H_{10}O_5N_2$: C, 61.9; H, 3.2; equiv. wt., 310. Found: C, 62.1; H, 3.0; equiv. wt., 311.

The acid is very sparingly soluble in ether and in methyl alcohol. It forms a colorless silver salt and a yellow copper salt which decomposes explosively when heated. Its solution in sodium carbonate does not reduce permanganate.

The Methyl Ester.—The ester, made through the silver salt, crystallized in very pale yellow prisms. Its melting point—133"—is the same as that of the methyl ester of the corresponding oxido acid but a mixture of the two substances melts at a much lower temperature.

Anal. Calcd. for $C_{17}H_{12}O_5N_2$: C, 62.9; H, 3.7. Found: C, 63.1; H, 4.1.

II. The Cyclopropene Derivative

For the purpose of getting an isomeric bromine compound the addition product was dissolved in a slight excess of methyl alcoholic sodium methylate and the resulting solution was added to an excess of bromine dissolved in methyl alcohol. This method generally gave an isomeric bromo compound that melted almost at the same temperature as the one that has been described, but all mixtures of the two invariably melted lower. In some cases the bromination resulted in a mixture of these bromo compounds. Since elimination of hydrogen bromide from the pure isomer gave the same two products that were obtained from the mixture, the latter was washed, dried and used without separation.

The Stereoisomeric Bromo Compound, II.—Forty-eight grams of the addition product was dissolved in a solution of 2.8 g. of sodium in 250 cc. of dry methyl alcohol. The orange-yellow solution was poured into 25 cc. of methyl alcohol containing an excess of bromine. The clear solution, on cooling, gradually deposited 46 g. of the monobromo compound, and an additional 3 g. was obtained from the mother liquors. The bromo compound separates from methyl alcohol, in which it is sparingly soluble, in small, almost colorless crystals that melt at 125–126°.

Anal. Calcd. for $C_{19}H_{17}O_8N_2Br$: C, 47.4; H, 3.5. Found: C, 47.2; H, 3.9.

Dimethyl 1-Phenyl-1-nitro-2-(3-nitrophenyl) Cyclopropane Dicarboxylate, IV.—A suspension of 50 g. of the bromo compound and 50 g. of potassium acetate in 300 cc. of dry ethyl alcohol was boiled for fifteen minutes, during which the bromo compound dissolved and the light yellow solution deposited both potassium bromide and cyclopropane derivative. The solution was filtered while hot. The first crop of solid, after washing with water until free from bromide and drying, weighed 11.5 g. It was almost pure cyclopropane derivative.

The filtrate from the first crop, on cooling, deposited 18.5 g. of a mixture of the oxide and the cyclopropane derivative. The mother liquor was diluted with water, extracted with ether—which removed a small quantity of oil and most of the color—and then acidified with a large excess of hydrochloric acid. The acid precipitated 2 g. of the isoxazole carboxylic acid (VIII).

The mixture of cyclopropane derivative and oxide was separated by dissolving in chloroform, in which it is very readily soluble, boiling the solution until the walls were entirely free from solid, and then inoculating it with pure oxide. It deposited 9 g. of almost pure oxide. The filtrate from the oxide yielded cyclopropane.

The cyclopropane diester is sparingly soluble in ether and in methyl alcohol. It crystallizes in colorless leaflets and melts at 167–169°.

Anal. Calcd. for $C_{19}H_{16}O_8N_2$: C, 57.0; H, 4.0. Found: C, 56.8; H, 4.3.

Action of Sodium Methylate, the Cyclopropene Diester, IX.—To a cold solution of 0.25 g. of sodium in 30 cc. of dry methyl alcohol was added 5 g. of finely pulverized cyclopropane derivative. The mixture was heated on a steam-bath until the cyclopropane derivative was replaced by a fine, light yellow crystalline precipitate. The time required for this was ten minutes. The liquid was cooled, the solid collected on a filter and thoroughly washed with water and alcohol. The product was 4 g. of nearly pure cyclopropene derivative. The filtrate deposited a colorless salt which proved to be sodium nitrite.

The cyclopropene derivative is sparingly soluble in nearly all solvents but can be recrystallized from acetone, from which it separates in small pale yellow crystals. It melts at 176–178°.

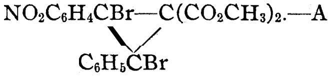
Anal. Calcd. for $C_{19}H_{15}O_6N$: mol. wt. 353; C, 64.6; H, 4.3; N, 4.1; OCH_3, 17.3. Found: mol. wt., 380; C, 64.4; H, 4.6; N, 4.2; OCH_3, 19.2.

The Cyclopropene Diacid, X.—The cyclopropane diester evidently loses nitrous acid more easily than any other nitrocyclopropane derivative that has been studied heretofore. When it is warmed with methyl alcoholic potassium hydroxide it not only undergoes hydrolysis but also loses nitrous acid. The product is the cyclopropene diacid. This acid is also formed when the cyclopropene diester is digested with methyl alcoholic potassium hydroxide. Since it is extremely soluble in methyl alcohol and very sparingly soluble in ether, it was purified by recrystallization from acetone and petroleum ether. From this mixture it separates in fine, colorless needles, containing one molecule of water of crystallization which is lost at 100°.

Anal. Calcd. for $C_{17}H_{11}O_6N{\cdot}H_2O$: C, 59.5; H, 3.8; N, 4.1; H_2O, 5.2; equiv., 171. Found: C, 59.4; H, 3.8; N, 4.4; H_2O, 5.1; equiv., 171.

The anhydrous acid melts at 216°. Esterification through the silver salt gave the calculated quantity of the ester from which it had been obtained.

Oxidation to Nitro Dibenzoyl Methane, XI.—The acid from 2 g. of the cyclopropene diester was dissolved in an excess of a 5% solution of sodium carbonate. To this canary-yellow solution, concentrated potassium permanganate solution was added in slight excess. After removing oxides of manganese with bisulfite and acid, there remained a gram of brownish colored solid which gave a gray-green copper derivative when its ethereal solution was shaken with aqueous copper acetate. The solid was recrystallized from acetone. The pure substance melted at 135–136°. Its melting point was not changed by admixture with a sample of nitro dibenzoyl methane in the usual way.[3]

Addition of **Bromine,**  $NO_2C_6H_4CBr—C(CO_2CH_3)_2$ C_6H_5CBr .—A small quantity of a dilute solution of bromine in chloroform was added to a solution of one gram of the cyclopropene ester in the same solvent. In diffuse daylight no reaction was perceptible but in direct sunlight the bromine disappeared. More bromine was added in the same manner as long as it disappeared. The excess bromine and the solvent were then removed under diminished pressure. The residue was a yellow oil which solidified when it was rubbed with ether and petroleum ether. The solid was recrystallized from methyl alcohol and water.

Anal. Calcd. for $C_{19}H_{15}O_6NBr_2$: C, 44.4; H, 2.9. Found: C, 44.4; H, 3.2

The dibromide is readily soluble in chloroform, in ether and in hot methyl alcohol, sparingly soluble in cold methyl alcohol, insoluble in petroleum ether. It crystallizes in colorless needles and melts at 144–145°. The yield was quantitative

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[3] Bodforss, *Ber.*, 49, 2803 (1916).

Action of Alkalies.—The dibromide is comparatively insensitive to bases but it slowly reacts with hot alkalies. Thus when 1.5 g. of the substance was boiled with excess of concentrated alcoholic potassium hydroxide it slowly dissolved and when the resulting dark colored solution was acidified it deposited a good yield of the cyclopropene di-acid. Toward concentrated alkalies, therefore, the dibromide behaves essentially like the cyclopropene dibromide discovered by Feist.[4]

The dibromide is also attacked slowly by dilute alkalies but the reaction, which is much more involved, has not yet been cleared up.

Summary

1. It is shown that cyclopropene derivatives can be obtained by eliminating nitrous acid from properly constituted nitro cyclopropane derivatives.
2. A method is described for preparing cyclopropene derivatives which differ from the few known heretofore in that they contain neither a conjugated system nor any hydrogen which by shifting could generate such a system.
3. It is found that the stability of cyclopropene derivatives is not dependent on the presence of a mobile hydrogen atom.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE REACTION BETWEEN MAGNESIUM DIPHENYL AND BROMINE. AN HISTORICAL NOTE ON THE FIRST PREPARATION OF PHENYLMAGNESIUM BROMIDE

BY HENRY GILMAN AND ROBERT E. BROWN

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Introduction

Long years ago Frankland[1] and Fleck[2] publicly called attention to the absence of organomagnesium halides. Fleck[2] purposefully set out to prepare phenylmagnesium bromide (by the *slow* addition of bromine to dry magnesium diphenyl covered with anhydrous ether) by the following reaction written by him

$$(C_6H_5)_2Mg + Br_2 \longrightarrow C_6H_5MgBr + C_6H_5Br \qquad (I)$$

However, because he obtained only bromobenzene and magnesium bromide he pictured the course of reaction as follows

$$(C_6H_5)_2Mg + 2Br_2 \longrightarrow 2C_6H_5Br + MgBr_2 \qquad (II)$$

and wrote, "One may assume that the latter reaction took place and that

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[4] Feist, *Ber.*, 26, 750 (1893).

[1] Frankland, *J. Chem. Soc.*, 13, 194 (1861).

[2] Fleck, *Ann.*, 276, 129 (1893). The results of these studies by Herman Fleck of Philadelphia, working in the laboratory of Lothar Meyer, were published in a dissertation at Tübingen in 1892.

a stable compound corresponding with the formula C_6H_5MgBr was not formed."

Incidental to studies on magnesium dialkyls and diaryls, we were curious to learn whether Fleck actually did have phenylmagnesium bromide in hand. Solely by analogy with other investigations in this Laboratory on organometallic compounds, it appeared altogether reasonable that phenylmagnesium bromide was an intermediate compound. However, it is an uncommonly difficult matter to make any chemical differentiation between phenylmagnesium bromide and a solution or mixture of magnesium diphenyl and magnesium bromide. This is so because we have not as yet come upon any chemical reaction of either of these compounds that is not shown by the other.

However, we believe that we have shown by a series of indirect proofs that Fleck actually did synthesize phenylmagnesium bromide as an intermediate step in his reaction.[3] As previously stated, there is not available at present any chemical reaction which can serve to differentiate unambiguously magnesium diphenyl from phenylmagnesium bromide. For example, after adding to magnesium diphenyl a quantity of bromine equivalent to that indicated in Reaction I, a simple but reliable test like the color test of Gilman, Schulze and Heck[4] is obtained. But there is no way of telling whether the positive color test obtained under such conditions is due to either one or both of the organomagnesium compounds, inasmuch as some of the one molecule of bromine may have reacted in accordance with both Reactions I and II, forming phenylmagnesium bromide and leaving some unaltered magnesium diphenyl—and each of these compounds gives the color test. In all this discussion it must be remembered that Fleck added an excess of bromine to the magnesium diphenyl, but he added it slowly, and sometimes in the course of the addition there was present in the reaction mixture one molecule or one equivalent of bromine in accordance with his Reaction I.

Two experiments served to prove that when one molecule of bromine is added, phenylmagnesium bromide is formed, and formed in accordance with Reaction I, to the probable exclusion of any unaltered magnesium diphenyl. First, it was shown that phenylmagnesium bromide reacts

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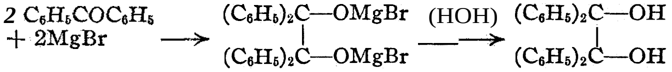
[3] We are not concerned here with any consideration of Fleck's priority. Fleck actually synthesized unknowingly the first organomagnesium halide; he knowingly set out to do so; but he equally definitely stated that a stable organomagnesium halide had not formed. Some credit is due Fleck for his early work. Whatever earlier work was done by others does not detract from the splendid and comprehensive studies by Professor Grignard. One of us (H. *G.)* in April, 1923, at the spring meeting of the American Chemical Society at New Haven, Connecticut, read a paper on this particular subject entitled "What Constitutes Discovery?"

[4] Gilman and Schulze, **This Journal, 47,** 2002 (1925); Bull. *soc. chim., 41,* 1479 (1927); Gilman and Heck, *Rec. trav. chim.,* **48,** 193 (1929); *Ber.,* 62, 1379 (1929).

much more readily with n-valeronitrile than does an equivalent solution of magnesium diphenyl.[5] With this as a basis, one molecule of bromine was added to magnesium diphenyl and a determination made of the rate of reaction of the resulting solution with n-valeronitrile. It was found that the solution formed in this way reacted almost exactly at the same rate as an equivalent solution of phenylmagnesium bromide (see Reaction I).

Second, if on the addition of one molecule of bromine a transformation occurs in accordance with Reaction I (but not in accordance with Reaction 11), then no magnesium bromide should be present. Fortunately, the recent studies by Gomberg and co-workers[6] make it possible to ascertain the presence of magnesium bromide. They showed that a mixture of magnesium bromide and magnesium behaves as though it were magnesious bromide (–MgBr), and that such an abnormally valenced complex reduces benzophenone to benzopinacol, as follows



$$\begin{matrix} 2\,C_6H_5COC_6H_5 \\ +\,2MgBr \end{matrix} \longrightarrow \begin{matrix} (C_6H_5)_2C\text{—}OMgBr \\ | \\ (C_6H_5)_2C\text{—}OMgBr \end{matrix} \xrightarrow{(HOH)} \begin{matrix} (C_6H_5)_2C\text{—}OH \\ | \\ (C_6H_5)_2C\text{—}OH \end{matrix} \qquad \text{(III)}$$

Accordingly if an excess of benzophenone and magnesium were added to a solution resulting from one molecule of magnesium diphenyl and one molecule of bromine, benzopinacol should form if any magnesium bromide were present. This is probably so even if three reagents (the magnesious bromide, magnesium diphenyl and phenylmagnesium bromide) were competing for but one molecule of benzophenone and not the excess we used. The reason for this is that Gomberg and Bachmann[6] have shown that magnesious iodide reacts more rapidly with benzophenone than does phenylmagnesium iodide, and our present studies show that phenylmagnesium bromide reacts more readily than magnesium diphenyl.[7]

The absence of magnesium bromide was established in an indirect manner. Even though one molecule of bromine might have reacted to some degree in accordance with Reaction II to give magnesium bromide, it is quite certain that the magnesium bromide so formed would react in turn with unaltered magnesium diphenyl, in accordance with the following reaction, to give phenylmagnesium bromide

[5] This is one of a number of semi-quantitative studies on the reaction rates of a variety of organometallic compounds. A preliminary account of these studies was read at the April, 1929, Meeting of the Iowa Academy of Science held at Pairfield, Iowa, and at the September, 1929, Meeting of the American Chemical Society held at Minneapolis, Minnesota. The difference in time of action illustrates the possibility of getting preferential reactions with magnesium diphenyl.

[6] See Gomberg and Bachrnann, THIS JOURNAL, 49, 236 (1927), and subsequent papers by Gomberg and co-workers.

[7] We should emphasize here that the more rapid reaction of phenylmagnesium bromide with n-valeronitrile does not justify any sweeping generalization to the effect that phenylmagnesium bromide will react more rapidly than magnesium diphenyl with any reagent.

$$(C_6H_5)_2Mg + MgBr_2 \longrightarrow 2\ C_6H_5MgBr \qquad (IV)$$

The correctness of Reaction IV was established by adding one molecule of magnesium bromide to one molecule of magnesium diphenyl and noting that the resulting solution when treated with magnesium and benzophenone gave no benzopinacol, thereby proving the absence or the disappearance of the magnesium bromide.[8] A like result was obtained with magnesium diphenyl and magnesium iodide. These experiments confirm earlier work by Gilman and Fothergill[9] on the constitution and dissociation of the Grignard reagent in which it was shown that magnesium diethyl reacts with magnesium iodide to give ethylmagnesium iodide, and that the transformation represented in Reaction IV is probably an equilibrium, with the equilibrium displaced almost completely to the right.

We have also shown that Fleck's Reaction II is correct when an excess of bromine is added, inasmuch as almost exactly *two* molecules of bromine react with one molecule of magnesium diphenyl to give a solution that contains neither magnesium diphenyl nor phenylmagnesium bromide. What Fleck did, therefore, was to first form phenylmagnesium bromide and then destroy it by continuing the addition of bromine to an excess.

Experimental Part

The magnesium diphenyl was prepared in accordance with the directions of Gilman and Brown,[10] and was free of mercury diphenyl, diphenyl and halogen. All operations were carried out in an atmosphere of dry nitrogen. Aliquots of the magnesium diphenyl in a mixture of ether and benzene were used for the several experiments. The concentration of magnesium diphenyl was determined quantitatively by the method of Gilman, Wilkinson, Fishel and Meyers.[11]

Rate of Reaction with *n*-Valeronitrile.—The time required for the disappearance of a positive color test[P] when 0.01 mole of phenylmagnesium bromide was treated with 2 cc. (2 g. or 0.024 mole) of n-valeronitrile in a total of 40 cc. of ether–benzene solution was between five and six minutes.[12]

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[8] There is, of course, the possibility that the magnesium bromide might combine in some loose manner with the magnesium diphenyl to give a complex like $(C_6H_5)_2Mg \cdot MgBr_2$. Such a complex might at the same time show all of the reactions of magnesium diphenyl and yet hold the magnesium bromide with a sufficient tenacity to prevent its reaction with magnesium and benzophenone to give benzopinacol. This we consider unlikely because the addition compound of benzophenone and magnesium bromide[6] can react with magnesium to give benzopinacol. Also, studies on the structure of RCOOMgX, and ROMgX and HOMgX compounds show that all of them at moderate temperature react with magnesium and benzophenone to give benzopinacol. The same is true of the pyridine complex with magnesium iodide.

[9] Gilman and Fothergill, THIS JOURNAL, 51, 3149 (1929).

[10] Gilman and Brown, *Rec. trav. chim.*, 49, (March, 1930).

[11] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, 45, 150 (1923). See also Gilman, Zoellner and Dickey, *ibid.*, 51, 1576 (1929), for improvements in this method of titration for the quantitative estimation of reactive organometallic compounds.

[12] In this procedure a small part of the reaction mixture is removed at stated intervals for the color test. For a general idea of the sensitiveness of this method see Gilman and Vanderwal, *Bull. soc. chim.*, 45, 344 (1929).

To a well-cooled solution of 0.01 mole of magnesium diphenyl was added 1.6 g. (0.01 mole) of bromine in an ether–benzene solution. After the misture had cooled to room temperature, 2 cc. of *n*-valeronitrile was added. The total volume of solution was again 40 cc. This reaction was complete in five minutes.

An ether–benzene mixture was added to a solution of 0.01 mole of magnesium diphenyl until the volume was 36 cc. Then 4 cc. of n-valeronitrile was added with rapid stirring, a procedure followed in the other rate experiments. The reaction was complete after about two *hours.* In order to make certain that the bromobenzene formed in accordance with Reaction I was without effect on the rate in the magnesium diphenyl experiment, 3.2 g. (0.02 mole) of bromobenzene was added to a magnesium diphenyl solution and the rate of reaction with n-valeronitrile measured as before. The time required for the disappearance of magnesium diphenyl was the same as that when no bromobenzene was present. Bromobenzene is also without effect on the rate of reaction between phenylmagnesium bromide and n-valeronitrile.

Magnesium Diphenyl with Magnesium Bromide and Magnesium Iodide.—There appeared to be no heat of reaction when 0.01 mole of magnesium iodide in an ether–benzene solution was added to 0.01 mole of magnesium diphenyl. On the subsequent addition of 0.3 g. (0.0125 atom) of powdered magnesium and 7.3 g. (0.04 mole) of benzophenone in 25 cc. of benzene, the solution became warm, and after about ten minutes the mixture cooled somewhat and a whitish-yellow precipitate formed in considerable quantity. The mixture was allowed to stand for several hours with frequent shaking. On the following day the contents of the flask had not changed in appearance. On working up the reaction mixture in a customary manner,[9] there was obtained 3.8 g. or 73% of triphenylcarbinol. No benzopinacol was found. In a corresponding experiment in which the magnesium iodide was replaced by magnesium bromide, the yield of triphenylcarbinol was 65%. Again no benzopinacol was found.[13]

Magnesium Diphenyl and Bromine.—A solution resulting from the reaction between 0.01 mole of bromine and 0.01 mole of magnesium diphenyl was carbonated after the procedure of Gilman and Parker.[14] The yield of benzoic acid obtained in this manner was 0.65 g. or 53%, which compares favorably with larger-sized runs with phenylmagnesium bromide.

A solution containing 3.2 g. (0.02 mole) of bromine in 50 cc. of an ether–benzene mixture was added to 0.01 mole of a magnesium diphenyl solution. After the addition of 45 cc. of the bromine solution, the reaction mixture still gave a positive color test.[4] However, when all (50 cc. or 0.02 mole) of the bromine solution was added, there was no color test.

Summary

When bromine is added to magnesium diphenyl, phenylmagnesium bromide is first formed. This is probably the first reported reaction in which an organomagnesium halide is formed in ether. However, Fleck, who originally carried out this reaction, overlooked the intermediate formation of phenylmagnesium bromide.

AMES, IOWA

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[13] The experiments with magnesium bromide and magnesium iodide were checked. The same was done with the rate determinations in the n-valeronitrile reaction with magnesium diphenyl and phenylmagnesium bromide, respectively.

[14] Gilman and Parker, THIS JOURNAL, 46, 2816 (1924).

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

EPOXY ACIDS FROM OLEIC AND ELAIDIC ACIDS[1]

BY BEN H. NICOLET AND THOMAS C. POULTER

RECEIVED NOVEMBER 5, 1929 PUBLISHED MARCH 6, 1930

The present work was undertaken to throw light on the effect of a long aliphatic chain on the reactivity of the ethylene oxide grouping. It also offered an opportunity to compare a pair of epoxides which were geometrical isomers.[2]

By the carefully controlled action of chlorine on solutions of the potassium salts containing potassium carbonate, relatively pure chlorohydrins (IIa, b) of oleic acid and of elaidic acid were obtained, though neither could be made to solidify.[3] The chlorohydrins, heated with alcoholic alkali, gave the epoxides (IVa, b), together with considerable amounts of unsaturated material which interfered seriously with the isolation of the desired products. The oleic acid chlorohydrin thus formed 45% (theoretical) of the epoxide, of which only a third could be isolated; the elaidic acid derivative yielded 75%, of which two-thirds could be separated. Both epoxides melted at 53.8.[4]

Our experience confirms the results of Albitzki, that both the chlorohydrin and the epoxide derived from oleic acid give on alkaline hydrolysis only the low-melting 9,10-dihydroxystearic acid. The corresponding derivatives from elaidic acid gave only the high-melting dihydroxy acid. It appears, however, that the epoxides are formed with such relative ease that with these *particular compounds* the hydrolysis of the chlorohydrins by alkali must take place almost exclusively by way of the epoxides.

While these epoxides react with water in the presence of alkali or of dilute acids only after hours of boiling, they add hydrogen chloride or sulfuric acid rather readily in ether solution at room temperature. When 0.1 N hydrogen chloride in dry ether was used, the reaction with elaidic acid epoxide was 90% complete after one hour at 20°; the oleic acid epoxide disappeared 3 or 4 times as rapidly. The products were chlorohydrins, each of which with alkali regenerated the same epoxide from which it had been formed. They were, however, readily obtained as solids, and appear to differ from the chlorohydrins formed by the addition of HOCl to the unsaturated

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[1] This material is taken from a thesis to be presented by Thomas C. Poulter to the Ogden Graduate School of Science in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The work was completed in 1926.

[2] Kuhn and Ebel, *Ber.*, 58, 919 (1925), have described the epoxides of maleic and fumaric acids. Their paper leaves us with no desire at present to try to distribute the labels cis and *trans* among the substances to be described by us.

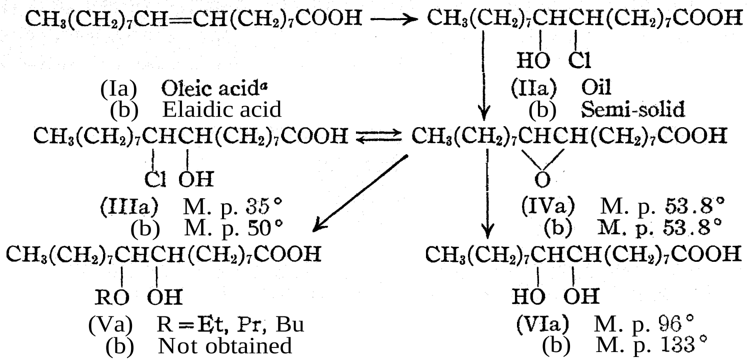
[3] Albitzki, *J. prakt. Chem.*, *61*, 65 (1900), describes oleic acid chlorohydrin as an oil, and elaidic chlorohydrin as a solid, m. p. 44–55".

[4] Albitzki, Ref. 3, describes them as an oil, and a solid of m. p. 57–60, respectively.

acids. The latter (IIa, b) are presumably 9-chloro-10-hydroxystearic acids. It is considered probable that the products obtained from the epoxides and hydrogen chloride are the isomeric 9-hydroxy-10-chlorostearic acids (IVa, b). The suggested relationships are indicated in Table I.

TABLE I

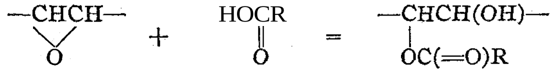
RELATIONSHIPS AND PROPERTIES OF CERTAIN COMPOUNDS



[a] No attempt is made to indicate steric relationships. The derivatives designated "a" and "b" are those obtained by the process indicated from oleic acid and elaidic acid, respectively.

An analytical method for the determination of the epoxides in mixtures was based on the reaction with hydrogen chloride in ether just described. By using a standard acid solution, allowing the reaction to go to completion and then determining the total acidity of the final solution, it was possible to determine the amount of hydrogen chloride which had disappeared in the reaction, and therefore the amount of epoxide initially present. Results consistent within 1% or less were readily obtained, and as neither the chlorohydrins nor the dihydroxystearic acids interfered, this method was very useful in following the reactions to be reported below.

Prolonged heating of the dry epoxides at 100–150° causes a reaction which leads in some hours to the complete destruction of the epoxide grouping, and simultaneously to the disappearance of much of the free carboxyl. After the epoxide has all reacted, the free carboxyl, now reduced to 25–50% of the initial value, remains constant on further heating. The chief reaction is thus apparently an addition of carboxyl at the epoxide group (probably, in general, of a different molecule) with the final formation of products of rather high and variable molecular weight. Here again the



$$\underset{\diagdown\,O\,\diagup}{-CHCH-} + \underset{\parallel \atop O}{HOCR} = \underset{|\atop OC(=O)R}{-CHCH(OH)-}$$

oleic acid epoxide reacts considerably more rapidly than its isomer. It is evident that other reactions also take place at the same time, since the carboxyl group does not disappear sufficiently completely to account for more than 50–75% of the epoxide disappearing.

At higher temperatures a different change becomes more prominent. Even on rapid distillation of small quantities at 10 mm., most of the epoxide does not distil unchanged. On slower distillation, or at higher temperatures, it disappears completely, giving a considerable quantity of 10-ketostearic acid, and usually a somewhat larger quantity of an unsaturated material which is presumably an hydroxyoleic acid of unknown constitution. Under parallel conditions the elaidic acid epoxide decomposes less rapidly, and gives a somewhat larger yield of the keto acid. The two 9,10-dihydroxystearic acids decompose much less readily on distillation than do the epoxides, but yield (at the higher temperatures required for their decomposition) the same ketostearic acid and presumably the same unsaturated hydroxy acid.

There are thus essentially three reactions of thermal decomposition of these epoxides: (A) hydroxy ester formation; (B) unsaturated hydroxy acid formation, which may possibly proceed through A, and (C) rearrangement to ketostearic acid.

When the epoxide of oleic acid is allowed to stand for two days in absolute alcohol containing 1% of concentrated sulfuric acid and the product then saponified, an ethoxyhydroxystearic acid (m. p. 87°) is formed. The corresponding n-propyl and n-butyl derivatives melt at 87–88° and 90°. The same process applied to elaidic acid epoxide yielded only dihydroxystearic acid, indicating that the sulfuric acid had added to the epoxide group, but that alcoholysis of the product had not taken place.

Esters of the epoxy acids themselves were not readily attainable by standard methods. The silver salts reacted extremely sluggishly with methyl iodide, and hydrogen chloride or sulfuric acid in alcohol attacked the epoxide group rapidly. The methyl esters were easily obtained in excellent yields when phosphorus pentoxide was added to the cooled solution of the epoxide in absolute methanol, and the product, after an hour, poured into water.

Experimental Part

9-Chloro-10-hydroxystearic Acids (IIa, b).—A 2% solution of potassium oleate (or elaidate) containing 4% of potassium carbonate was cooled below 10" and stirred while chlorine was passed in until the iodine number[5] was less than 1.0. Excess hypochlorite was destroyed with sodium thiosulfate before acidification. Oleic acid chlorohydrin was a viscous oil.

Anal. (Carius). Calcd. for $C_{18}H_{35}O_3Cl$: Cl, 10.6. Found: Cl, 10.23.

Elaidic acid chlorohydrin was a semi-solid, but could not be crystallized.

Oleic Acid Epoxide (ma).—The chlorohydrin was refluxed for two hours with

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[5] The Wijs iodine numbers of the chlorohydrins, the epoxides and the dihydroxystearic acids here discussed were negligible.

excess of molar sodium ethylate in 95% alcohol. The solution was then poured into 10 volumes of cold water, the acid liberated with hydrochloric acid and crystallized from methanol. It melts at 53.8°; samples have been kept for four years practically unchanged; on the other hand, certain other samples have become salve-like and developed a rancid odor in less than a year.

Anal. (Titration). Calcd. for $C_{18}H_{34}O_3$: equiv. wt., 298.3. Found: 296, 300.

The yield of pure product was about 15%. The oily residue contained 35–40% of epoxide which we could not isolate. This oil also contained (in various preparations) 1–3% of chlorine and had an iodine number of 10–25.

Elaidic Acid Epoxide (IVb).—The chorohydrin of elaidic acid was treated as described above. This epoxide also melts at 53.8°, but a mixture of the two epoxides melts at 45–47'. The yield was 45–50% and the oily residue still contained about 50% of epoxide.

Anal. (Titration). Calcd. for $C_{18}H_{34}O_3$: equiv. wt., 298.3. Found: 297, 300.

Both epoxides were more than 99% pure, as determined by their absorption of hydrogen chloride.

Action of Peracids on Oleic and Elaidic Acids.—In the hope of obtaining the desired epoxides more directly, the action of perbenzoic acid in chloroform,[6] on oleic and elaidic acids was tried. In each case the dihydroxystearic acid to be expected from the hydrolysis of the epoxide (m. p. 96 and 133°, respectively) was the only solid product isolated. Peracetic acid[1] gave entirely similar results.

9-Hydroxy-10-chlorostearic Acids (IIIa, b).—Oleic acid epoxide was dissolved in at least twice the calculated volume of a solution of hydrogen chloride (ca. 0.2 N) in dry ether. After an hour at room temperature, the excess hydrogen chloride was removed by washing the ether solution with water. Evaporation of the ether gave the hydroxychlorostearic acid as an oil which after several days solidified; m. p. 35°. By the same process elaidic acid epoxide gave an isomeric hydroxychlorostearic acid; m. p. 50°.

Anal. Calcd. for $C_{18}H_{35}O_3Cl$: equiv. wt., 334.7; Cl, 10.59. Found for acid of m. p. 35°: equiv. wt., 335.7; Cl, 10.2. Found for acid of m. p. 50°: equiv. wt., 336; Cl, 10.8.

Each of the 9-hydroxy-10-chlorostearic acids regenerates, when warmed with alcoholic alkali, the same epoxide from which it was made.

Methyl Esters of the Two Epoxides.—The silver salts of the epoxy acids reacted extremely slowly with alkyl iodides. On the other hand, attempts to catalyze esterification with hydrochloric or sulfuric acid led to rapid destruction of the epoxide ring.

TABLE II

PROPERTIES AND ANALYSES OF METHYL ESTERS

Methyl ester of	M. p., °C.	Equivalent weight by saponification Formula	Calcd.	Found
Oleic acid epoxide	18	$C_{19}H_{36}O_3$	312	313.7
Elaidic acid epoxide	25	$C_{19}H_{36}O_3$	312	312.6
9,10-Dihydroxystearic acid (m. p. 96°)	63	$C_{19}H_{38}O_4$	330	331.3
9,10-Dihydroxystearic acid (m. p. 133°)	97	$C_{19}H_{38}O_4$	330	330.9
10-Ketostearic acid	43	$C_{19}H_{36}O_3$	312	311.1

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[6] Pigolevskii and Petrov, J. *Russ. Phys.-Chem. Soc.*, *58,* 1062–1066 (1926); C. *A.*, 22, 943 (1928), obtained among other products the epoxide of oleic acid by the use of benzoyl peroxide (?) in ether

[7] Hilditch and Lea, J. *Chem. Soc.*, 1576–1583 (1928), found no indication of epoxide formation by hydrogen peroxide in acetic acid with methyl oleate or elaidate.

Phosphoric acid seems not to behave in this manner. To 2 g. of the organic acid in 75 cc. of absolute methanol, 2 g. of phosphorus pentoxide was added and the mixture cooled and shaken until solution was complete. After an hour it was poured into 10 volumes of cold water, and the ester separated by filtration or, if liquid, by extraction with ether. The yields were very good. Table II gives the melting points and equivalent weights by saponification of a number of esters thus obtained. All were recrystallized from methanol and each regenerated the original acid when saponified.

Alcoholysis of Oleic Acid Epoxide. Monoalkyl Ethers of (Low Melting) 9,10-Dihydroxystearic Acid.—Oleic acid epoxide was dissolved in 25 parts of absolute ethanol containing 1% of sulfuric acid and allowed to stand for two days. The solution was poured into excess aqueous alkali and heated to saponify the ester formed, allowing the alcohol to evaporate. When the cooled solution was poured into an excess of dilute hydrochloric acid, the acid separated and was recrystallized from ether. Analogous products were obtained by the use of absolute propyl and n-butyl alcohols. The melting points and titrations are given in Table III.

TABLE III

PROPERTIES AND ANALYSES OF 9,10-ALKOXY-HYDROXYSTEARIC ACIDS

Monoalkyl ether	M. p., °C.	Formula	Equiv. wt. by titration Calcd.	Equiv. wt. by titration Found
(a) Ethyl	87	$C_{20}H_{40}O_4$	344	340
(b) n-Propyl	87–88	$C_{21}H_{42}O_4$	358	351
(c) n-Butyl	90	$C_{22}H_{44}O_4$	372	366

Mixtures of a and b, a and c, and b and c, all melted at about 85°.

Attempts to apply the same procedure to elaidic acid epoxide gave in every case only the dihydroxystearic acid of m. p. 133°. Under somewhat more severe conditions, the alcoholysis might be successful.

Quantitative Determination of the Epoxides.—The absorption of hydrogen chloride by the epoxides in dry ether has been discussed. An analytical method was based on this reaction.

A 0.1–0.2 N solution of hydrogen chloride in dry ether was prepared and standardized. The sample of epoxide was dissolved in a measured volume of this solution containing at least twice the amount of hydrogen chloride theoretically necessary, allowed to stand for two hours at room temperature in a stoppered flask, then poured into neutralized alcohol and titrated with standard potassium hydroxide solution, using phenolphthalein. The alkali equivalent of the fatty acid used must be separately determined on another sample. The acid which disappears in the reaction (hydrogen chloride) is reported as moles of epoxide. The dihydroxystearic acids and 10-ketostearic acid do not interfere. Results within 1% could be obtained with known mixtures.

This method was used to determine the epoxides in the various experiments to be reported on the (approximate) rates of reaction of these substances.

Relative Reactivities of the Two Epoxides toward Hydrogen Chloride.—Appropriate titrations showed that in 0.1 N ethereal hydrogen chloride at 20°, elaidic acid epoxide reacted to the extent of 90% in one hour. The oleic acid epoxide reacted at least three times as rapidly.

Relative Rates of Hydrolysis to Dihydroxystearic Acids.—On boiling with 1% aqueous hydrochloric or sulfuric acid, the epoxides of oleic and elaidic acids gave the dihydroxystearic acids (m. p. 96 and 133°, respectively). The oleic epoxide reacted decidedly the more rapidly, but the hydrolysis requires many hours even in this case.

The comparison in alkaline solution is more significant, as the question of solubility does not here arise. A 2% solution of the epoxide in 2 N potassium hydroxide was heated at 100° and the unaltered epoxide determined from time to time by the method described. Hydrolysis took place at the rates of about 11 and 3.5% an hour for the oleic and elaidic acid epoxides, respectively.

Reactions of the Dry Epoxides

Effect of Heating at 114 and 150°.—At either temperature, the dry epoxides decomposed over a period of some hours. At intervals samples were titrated for unchanged epoxide and for free acid. As usual the elaidic acid epoxide proved to be the more stable. The results are given in Table IV; their interpretation has already been discussed. Attention is called to the fact that, after the disappearance of the epoxide, acidity remains constant.

TABLE IV

RESULTS OF HEATING THE EPOXIDES

Time, hrs.	Temp., °C.	Oleic acid epoxide		Elaidic acid epoxide	
		Epoxide, %	Free acid, %	Epoxide, %	Free acid, %
0	114	100	100	100	100
1	114	40	66	83	94
3	114	13	55	70	86
8	114	0	50	35	71
17	114	0	50	8	56
22	114			0	53
40	114			0	53
0	150	100	100	100	100
1	150	24	37	50	78
2	150	10	26	25	64
3	150	4	24	9	56
4	150	0	23	0	53
5	150	0	23	0	53

Effect of Higher Temperatures.—On distillation, even at 10 mm. (*ca.* 290") and in small quantities, the epoxy acids are largely decomposed. A 4-g. sample of oleic acid epoxide thus distilled (during about ten minutes) gave a product with an iodine number of 62, containing only 17% of epoxide and some 10-ketostearic acid. Under as nearly parallel conditions as possible, the distillate from elaidic acid epoxide had an iodine number of 10, contained 40% of unchanged epoxide, and a somewhat larger proportion of ketostearic acid than in the former case.

Summary

1. The epoxides of oleic and elaidic acids have been obtained in crystalline form.
2. The splitting of the epoxide ring by hydrogen chloride, water and alcohol has been investigated.
3. Three directions in which these epoxy acids decompose on heating have been discussed.
4. In all the reactions considered, the oleic acid epoxide is the less stable, and reacts in general from two to four times as rapidly as does its isomer.
5. A method for the quantitative determination of these epoxides has been described.

RIVERDALE, MARYLAND

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE BUREAU OF DAIRY INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

INTERPRETATION OF THE DEHYDRATION OF ACETYLGLUTAMIC ACID BY MEANS OF GLUTAMYLTHIOHYDANTOIN DERIVATIVES

BY BEN H. NICOLET

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Bergmann, Stern and Witte[1] have shown that azlactones formed by the simultaneous acetylation and dehydration of the acetyl derivatives of certain amino acids may be coupled with other amino acids to yield acetyl dipeptides. In the case of acetyl-aspartic acid they considered,[2] without appreciable evidence, that the dehydration product was an acetylaspartic anhydride, rather than an azlactone. In any case, they isolated the product, and obtained from it by the action of glycine ester in ether solution a substance having the empirical formula of a glycine ester salt of acetylaspartylglycine. No evidence was presented as to which carboxyl group was concerned in the formation of the dipeptide.

The desirability of a new synthesis of glutathione has led to work here on the possibility of obtaining derivatives of the glutathione[2a] type (γ-glutamyldipeptides) by an analogous process. The work has not yet progressed so far as this, but the evidence here given indicates that the desired reactions should take place.

Glutamic acid is so insoluble even in boiling acetic anhydride that it is not practicable to acetylate it directly. On the other hand, acetylglutamic acid (II) is formed in fairly good yield when acetic anhydride in moderate excess is added to a water solution of sodium glutamate.[3] When the solution is sufficiently concentrated, the product separates on acidification and cooling.

On warming with acetic anhydride, acetylglutamic acid dissolves readily and is dehydrated. When the excess acetic anhydride is removed by distillation under reduced pressure, and the residual oil treated with an excess of aniline, a product (VI) results which on condensation with ammonium thiocyanate and acetic anhydride[4] yields 1-acetyl-2-thiohydantoin-5-β-propionanilide (VII) in 34% yield. The dehydration might reasonably have taken place in either of two ways, with the production of the anhy-

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[1] Bergmann, Stern and Witte. *Ann.*, 449, 279 (1926).

[2] Ref. 1, pp. 301–302.

[2a] At the time this paper was written the glutamylcystine structure for glutathione was accepted. Later evidence [Hopkins, *J. Biol. Chem.*, 84, 269 (1929); Kendall, McKenzie and Mason, *ibid.*, 84, 657 (1929)] shows that glutathione is a tripeptide. The type of combination, however, remains the same.

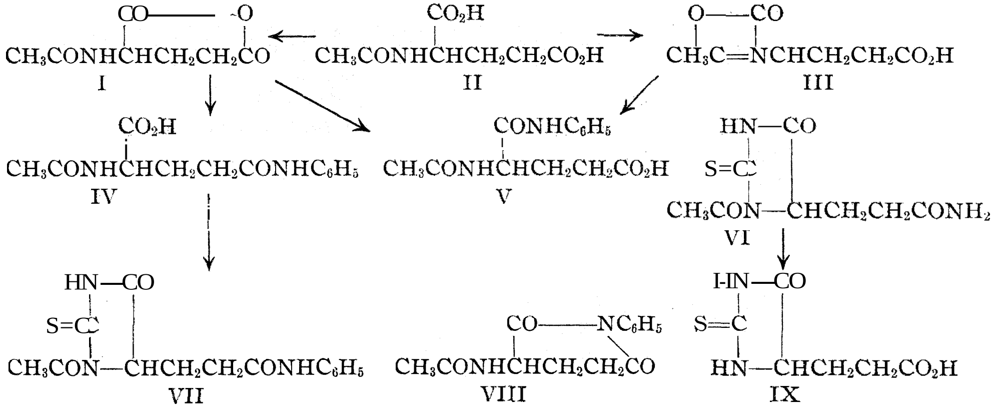
[3] Other amino acids can also be acetylated under these conditions.

[4] Johnson and Nicolet, *Am. Chem. J.*, 49, 197–204 (1913).

dride I or of the azlactone III. The addition of aniline, in turn, might have yielded either of the two acetylglutamic acid monoanilides (IV and V). The anilide V might have resulted from either the azlactone or the anhydride; it could not have formed a thiohydantoin, and it was not detected, The anilide IV could have been formed only through one of the two possible modes of addition to the true anhydride. The formation of the thiohydantoin VII demonstrates the formation of the anilide IV (and therefore of the anhydride I) and indicates this particular anilide as at least the chief product of the reaction.

TABLE I

FORMULAS AND RELATIONSHIPS OF COMPOUNDS DESCRIBED



When acetylglutamic anhydride, prepared as above, was dissolved in aqueous ammonia, and the solution evaporated to dryness and condensed with thiocyanate as described, the product was 1-acetyl-2-thiohydantoin-5-β-propionamide (VI).[5]

Johnson and Guest[6] have described an indirect synthesis of glutamylthiohydantoin (IX), through pyrrolidonecarboxylic acid. They reported that on attempting to condense glutamic acid directly with thiocyanate solution took place, but the acid was de-aminated. Some such effect might account for the fact that the yield of VII obtained in this work was not larger. It seems, however, more probable that a partial dehydration of the acetylglutamic anilide IV to give the cyclic phenylimide derivative (VIII) (which would not be expected to yield a thiohydantoin) was responsible.

The thiohydantoin VII, dissolved in normal alkali and after half an

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[5] Thierfelder, *Z. physiol. Chem.*, 114, 192 (1921), obtained the hydantoin VI (m. p. 209°) in 22–30% yield from glutamin, and thereby proved the structure of the latter to be $HOOCCH(NH_2)CH_2CH_2CONH_2$. He also converted his VI to IX. His paper was discovered only after the present paper was written.

[6] Johnson and Guest, *Am. Chem. J.*, 47, 242 (1912).

hour re-acidified, readily lost its acetyl group[7] and formed 2-thiohydantoin-5-β-propionanilide. The hydantoin VI was also easily de-acylated by this method, but the product was too soluble for easy isolation. On further hydrolysis with hydrochloric acid, the final product melted at 122°, and was presumably identical with the glutamylthiohydantoin IX of Johnson and Guest.

Experimental Part

Acetylglutamic Acid (II).[8]—*d*-Glutamic acid (14.7 g., 0.1 mole) was dissolved in 34 cc. (0.2 mole) of 6 *M* sodium hydroxide. To the cold solution was added 15 cc. of acetic anhydride, and the mixture shaken under the tap until the anhydride dissolved. The solution was then acidified with 17 cc. of 12 M hydrochloric acid and left in the ice box for some time to crystallize. The crude product (about 10 g.) was recrystallized from a little water to remove sodium chloride. A further quantity was obtained when the mother liquors were evaporated to dryness (at 15–20 mm.), the large residue of salt extracted with alcohol, the extract evaporated and the residue purified from water as described. The total yield was then about 75%. It was also found feasible to isolate the product by repeated extraction of the aqueous salt solution with iso-amyl alcohol. Extraction with ether is not effective.

Pure acetylglutamic acid (m. p. 193–194°) is readily soluble in water and alcohol and, on warming, in acetic anhydride.

Anal. (Micro-Kjeldahl) Calcd for $C_7H_{11}O_5N$: N, 7.41. Found: N, 7.61.

Acetylglutamic Anhydride (I).—Acetylglutamic acid was heated for three minutes to boiling, or for thirty minutes at 100°, with 10 parts of acetic anhydride, and the solution evaporated at 20–30 mm. pressure. The anhydride remained as a viscous oil, readily soluble in organic solvents, except benzene, and only slowly soluble in water with formation of acetylglutamic acid.

1-Acetyl-2-thiohydantoin-5-β-propionanilide (VII).—Acetylglutamic acid (0.01 mole) was converted to the anhydride, and the excess acetic anhydride removed as completely as possible. Twice the calculated amount of aniline was then added, and the mixture, which became warm, was allowed to stand for an hour. Dry ammonium thiocyanate (1.0 g.) and acetic anhydride (8 cc.) were then added, and the mixture heated for one and one-half hours on the steam-bath. It was then cooled and poured into water, from which the solid product presently separated. A further small quantity was obtained from the mother liquors; the total yield was 0.9 g., or 34%. The pure substance, m. p. 197°, is moderately soluble in hot glacial acetic acid, rather difficultly soluble even in hot alcohol, and nearly insoluble in water.

Anal. (Micro-Kjeldahl). Calcd. for $C_{14}H_{15}O_3N_3S$: N, 13.77. Found: N. 14.0.

2-Thiohydantoin-5-β-propionanilide.—The acetyl derivative (0.2 g.) was dissolved in 10 cc. of molar sodium hydroxide. The solution, after standing for half an hour at room temperature, was acidified with hydrochloric acid and the bulky precipitate crystallized from alcohol. The pure substance darkened slowly above 200°, but melted at 216° with only slight decomposition.

Anal. (Micro-Kjeldahl). Calcd. for $C_{12}H_{13}O_2N_3S$: N, 15.95. Pound: N, 15.90.

1-Acetyl-2-thiohydantoin-5-β-propionamide (VI).—Acetylglutamic anhydride was

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[7] Schlack and Kumpf, Z. *physiol. Chem.*, *154*, 131 (1926), have called attention to this easy method for the de-acylation of 1-acylthiohydantoins, which seems to be quite general.

[8] All the substances described in this paper are derivatives of d-glutamic acid.

prepared as described above and treated with an excess of 6 *M* ammonium hydroxide solution. The anhydride rapidly dissolved. The solution was evaporated to dryness under reduced pressure and the residue condensed with ammonium thiocyanate and acetic anhydride as described for the corresponding anilide. A little water (5 *cc.*) was added to destroy the excess acetic anhydride and the solution was again evaporated nearly to dryness under reduced pressure. On addition of water, the product separated. It was difficultly soluble in cold water, and could be conveniently crystallized from hot water, in which its solubility was about 1%; m. p. 208–209°.

Anal. (Micro-Kjeldahl). Calcd. for $C_8H_{11}O_3N_3S$: N, 18.35. Found: N, 18.51.

Summary

1. Some new thiohydantoin derivatives of glutamic acid are described. Their formation is considered to show that the dehydration of acetylglutamic acid by acetic anhydride forms the true acetylglutamic anhydride, and not an azlactone.

2. When this anhydride reacts with amines, amide formation takes place at the carboxyl group most distant from the amino group. It is planned to extend the application of this reaction to the synthesis of γ-glutamyldipeptides.

BELTSVILLE, MARYLAND

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY AND THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

A GENERAL METHOD FOR THE DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS[1]

BY J. J. THOMPSON AND U. O. OAKDALE

RECEIVED NOVEMBER 6, 1929 PUBLISHED MARCH 6, 1930

Halogen in an organic compound is determined, usually, by the Carius[2] or by the Lemp and Broderson[3] modification of the Parr[4] and Pringsheim[5] methods.

The Carius procedure suffers from a number of disadvantages, namely, the use of a sealed tube the preparation of which requires considerable skill, the use of a bomb furnace in which to heat the tube and the danger of glass splinters falling into the tube when the latter is opened. It requires a number of hours to perform an analysis and it is not always an easy matter to determine when the sample is completely oxidized.

The disadvantageous features of the Lemp and Broderson process are the possibility of incomplete fusion, the danger of rapid oxidation when

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[1] This investigation was made possible by a grant from the Faculty Research Fund of the University of Michigan.

[2] Carius, *Ann.*, 136, 129 (1865).

[3] Lemp and Broderson, THIS JOURNAL, 39, 2069 (1917).

[4] Parr, *ibid.*, 30, 764 (1908).

[5] Pringsheim, *Am. Chem. J.*, 41, 386 (1904).

the sample is mixed with sodium peroxide and the difficulty of obtaining accurate results with very volatile compounds.

In the method to be described fuming sulfuric acid alone or in conjunction with chromic acid or a persulfate is used as the oxidizing agent instead of nitric acid or sodium peroxide. The process is carried out in an open apparatus of simple construction; hence all danger of explosion is eliminated. Since relatively large samples, 1 to 1.5 g. may be used, an unusual degree of accuracy can be attained. The oxidation of the sample is complete in a short time and the variety of compounds analyzed illustrates the general adaptability of the method. Very satisfactory results were obtained with such volatile compounds as ethyl bromide and with compounds difficult to oxidize such as chlorobenzene.[6] Moreover, in the event that the compound contains, in addition to halogen, metals such as mercury, arsenic, antimony or bismuth the latter can be determined readily as we have shown.

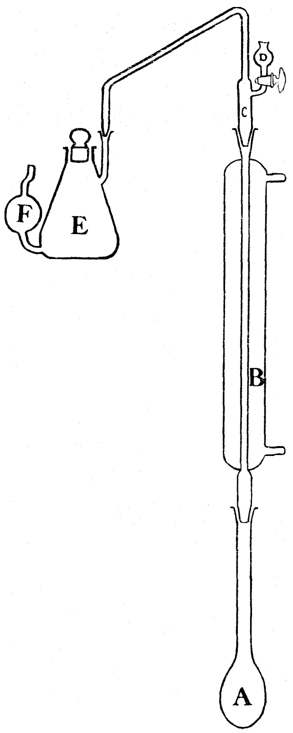

Fig. 1.

General Procedure.—The apparatus, made entirely of pyrex glass (Fig. 1),[7] consists of a 300-cc. Kjeldahl flask (A) fitted with a condenser (B), 69 cm. long, by means of a ground-glass connection.[7a] The tube C is attached to the top of the condenser by means of a ground-glass joint. The total length of the vertical part of this tube is 15 cm., the length of the oblique part is 20 cm. D represents a bulb of 10-cc. capacity, E a 250-cc. Erlenmeyer flask to which a safety bulb F of 100-cc. capacity is connected. All ground glass connections should be coated with phosphorus pentoxide.[7b] The sample is placed in the Kjeldahl flask and sulfuric acid is added through the dropping funnel. The liberated halogen passes through the condenser and is absorbed and reduced to halide in the Erlenmeyer flask, which contains an alkaline solution of sodium arsenite.8 The halide can be determined either gravimetrically or by the Volhard method. For very accurate results the gravimetric method should be used.

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[6] The results obtained in the case of chloroform and carbon tetrachloride were somewhat too low. This is due, undoubtedly, to the fact that some volatile organic halide is formed and is not hydrolyzed completely by the alkali in the absorption flask. By means of a slightly modified procedure, to be mentioned in a subsequent paper, entirely satisfactory results can be obtained in the case of the above-mentioned compounds.

[7] This apparatus can be purchased from the Arthur H. Thomas Co., Philadelphia.

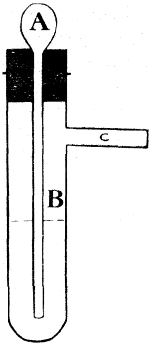
[7a] The ground-glass connections are held together by means of glass hooks, not shown in the figure, which are sealed to the apparatus.

[7b] Stephens, THIS JOURNAL, 52, 635 (1930).

[8] Hönigschmid and Zintl, *Ann.*, **433**, 201 (1923), have shown that alkaline arsenite is the best reducing agent for free halogen.

In the event that liquid material is to be analyzed, thin-walled glass bulbs are prepared A bulb is filled by placing it and the liquid sample in the apparatus shown in Fig. 2 The apparatus is evacuated through the side arm and then, upon allowing air to enter the apparatus, the bulb is filled automatically.

Determination of **Iodine.**[9]—After the sample, approximately one g, has been placed in the flask and 100 cc of 10% sodium hydroxide solution, which contains about I g. of arsenious oxide, has been poured into the Erlenmeyer flask, 20 cc. of fuming sulfuric acid, containing 20–30% of sulfur trioxide, is added slowly through the dropping funnel The mixture is boiled very gently for thirty minutes. During this time a rapid stream of water should flow through the condenser and no sulfur trioxide vapors should pass through the absorption flask. Thirty-five cc. of 95% sulfuric acid is added and the mixture boiled vigorously until it becomes colorless. Fifty cc. of water is added cautiously to the mixture, which should be kept at the boiling point to insure complete mixing. The water is then drained from the condenser, a small quantity of 30% hydrogen peroxide (Superoxol) is added carefully and the liberated iodine is driven through the condenser by boiling the solution. The addition of hydrogen peroxide and the heating are continued intermittently until all of the iodine has been liberated and absorbed. Ten cc. of peroxide is usually sufficient. It is advisable as a matter of routine practice to add, after the liberation of iodine is thought to be complete, about 5 cc. of a saturated solution of hydrazine sulfate. Any iodate which may have been formed is thus reduced. The mixture should be boiled for five minutes and hydrogen peroxide added to expel any iodine. The apparatus should be disconnected immediately to prevent "freezing" of the ground-glass connections. The contents of the absorption flask are now transferred to a 600-cc. beaker and carefully acidified with dilute nitric acid, methyl orange being used as the indicator. The iodide is precipitated by the addition of excess silver nitrate solution, then an excess of 5–10 cc. of concd. nitric acid is added to prevent the contamination of the silver halide with other silver salts. The solution is boiled until the silver iodide has coagulated. The precipitate is filtered into a weighed crucible, washed with 2% nitric acid solution, then with water and finally with acetone. The crucible is next dried at 130°. The time required for a complete analysis is 70–90 minutes.



The results obtained with various purified iodine compounds and analyzed inorganic reagents are shown in Table I.

Determination of Chlorine and **Bromine.**—For compounds which contain chlorine or bromine the procedure is the same as described above except for the following variations. If the substance to be analyzed contains no metallic element, 0.5 g. of copper sulfate is placed in the Kjeldahl flask. Furthermore, after the sample has been heated for thirty minutes, a suspension of 10 g. of potassium persulfate[9a] in 20 cc. of 95% sulfuric acid is added through the dropping funnel. Any material which adheres to the condenser is washed into the flask with 15 cc. of 95% sulfuric acid. The mixture is boiled vigorously until the green color of the copper sulfate is pronounced. After draining the water from the condenser an excess of concd. potassium permanganate solution is

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[9] The decomposition of an organic iodide with concentrated sulfuric acid and absorption of the liberated iodine was carried out without much success by Van Itallie, *Pharm.* Weekblad, 66, 629 (1929).

[9a] Since much of the persulfate on the market is contaminated with perchlorate it is essential to make a blank determination, with starch as the organic material, according to the method outlined here for chlorine.

TABLE I[a]

DETERMINATION OF IODINE

Compound	Formula	I present, %	I found,[b] %	Error
Diphenylarsyl iodide	$C_{12}H_{10}AsI$	35.65	35.54	−0.11
Iodoform	CHI_3	96.67	96.71	+ .04
p-Iodo-anisole	C_7H_7OI	54.24	54.19	− .05
β-Iodonaphthalene	$C_{10}H_7I$	49.97	49.82	− .15
Diphenylstibyl iodide[c]	$C_{12}H_{10}SbI$	31.51	31.42	− .09

[a] In this table, as well as in those which follow, the analytical results were obtained gravimetrically. [b] Each of these results, as well as those recorded in the following tables, represents the average of two duplicates agreeing to within 0.00–0.08%. [c] In the case of diphenylarsyl iodide the iodine can be determined by hydrolysis of the iodide with alcoholic sodium hydroxide and determination of the iodine by the Volhard method. With diphenylstibyl and diphenylbismuthyl iodide, however, this procedure is not applicable since a volatile organic iodide, presumably iodobenzene, escapes from the alkaline mixture when it is heated.

added to the boiling solution and the mixture is boiled for about five minutes to expel any chlorine or bromine which may remain in the flask or condenser. In order to determine the amount of absorbed chlorine or bromine the procedure described above is used. A complete analysis can be made in 70–90 minutes.

In the case of chlorobenzene, a substance difficult to oxidize, decomposition by means of sulfuric acid and potassium persulfate requires considerable time. However, if 5 *g.* of chromic acid is placed in the flask with the sample and fuming sulfuric acid is then added, in the usual manner, the compound can be oxidized rapidly. The addition of persulfate or permanganate is unnecessary but an excess of chromic acid must be present when the oxidation is complete. In the event that a compound proves difficult to decompose by means of sulfuric acid and potassium persulfate, a suspension of chromic acid in concd. sulfuric acid may be added through the dropping funnel.

Organic iodine compounds are decomposed much more readily than chloro derivatives.

When an organic compound which contains chlorine and mercury is decomposed, the chlorine is not liberated quantitatively, since the mercuric chloride which is produced unites with the sulfuric acid to form $HgCl_2 \cdot H_2SO_4$. In order to decompose the latter compound, 5 g. of granulated zinc, which reduces the mercury to an amalgam, is mixed with each gram sample before adding the fuming sulfuric acid.

TABLE II

DETERMINATION OF CHLORINE AND BROMINE

Compound	Formula	Cl present, %	Cl found, %	Error
o-Hydroxyphenylmercuric chloride	C_6H_5OHgCl	10.79	10.81	0.02
p-Chloro-acetanilide	C_8H_8ONCl	20.94	20.90	.04
p-Chlorobenzoic acid	$C_7H_5O_2Cl$	22.65	22.70	.05
Chlorobenzene	C_6H_5Cl	31.51	31.47	.04
2,4-Dinitrochlorobenzene	$C_6H_3O_4N_2Cl$	17.50	17.51	.01
		Br present, %	Br found, %	
p-Bromo-acetanilide	C_8H_8ONBr	37.34	37.41	0.07
p-Nitrobenzyl bromide	$C_7H_6O_2NBr$	37.00	36.99	.01
β-Bromopropionic acid	$C_3H_5O_2Br$	52.25	52.24	.01
9,10-Dibromo-anthracene	$C_{14}H_8Br$	47.58	47.51	.07
Bromobenzene	C_6H_5Br	50.91	50.90	.01
Ethyl bromide	C_2H_5Br	73.33	73.33	.00

In order to determine arsenic in diphenylarsyliodide, the residual solution, obtained after decomposition of the sample, liberation and absorption of the iodine, is concentrated and the pentavalent arsenic reduced to the trivalent state by boiling the solution with hydrazine sulfate.[10] The concd. sulfuric acid solution is heated above 254" in order to destroy excess hydrazine, then diluted and the sulfur dioxide, formed by decomposition of the hydrazine sulfate, boiled off. Ten cc. of hydrochloric acid is added and the arsenic trioxide titrated, at 80°, with $N/10$ potassium bromate, using methyl orange as the indicator.'' The arsenic may also be determined by the same procedure, without concentration of the solution, after reduction of the arsenic pentoxide with sulfur dioxide.

Antimony is determined in diphenylstibyl iodide in the following manner. The residual liquid in the Kjeldahl flask is transferred to a 250-cc. Erlenmeyer flask. The antimony salt is reduced to the trivalent state with sulfur dioxide, the solution diluted and boiled to remove excess sulfur dioxide. Ten cc. of concd. hydrochloric acid is added and the solution titrated, at 60°, with $N/10$ potassium bromate, using methyl orange as the indicator.

Diphenylbismuthyl iodide can be analyzed for bismuth[12] as follows. The residual sulfuric acid solution in the Kjeldahl flask is poured into a 400-cc. beaker, diluted and then treated with an excess of concd. ammonia water. The mixture is boiled in order to coagulate the bismuth hydroxide. The latter is filtered and washed several times with dilute ammonium hydroxide and dissolved in 20 cc. of concd. nitric acid. After dilution to 200 cc., the solution is heated to the boiling point and 3 cc. of a 10% solution of phosphoric acid added.[13] After the addition of rosolic acid, a 10% solution of trisodium phosphate is added. very slowly, to the boiling solution. The precipitate of bismuth phosphate is then filtered through a filtering crucible and washed with 1% ammonium nitrate solution which contains a drop of nitric acid per 100 cc. The precipitate is dried at 300°, ignited at the full heat of a Bunsen burner for five minutes and weighed as $BiPO_4$. The bismuth may also, but less accurately, be determined as bismuth trioxide.[14] The nitric acid solution is diluted to 300 cc. and dilute ammonium hydroxide is added until a faint turbidity is obtained. After the addition of excess ammonium carbonate, the solution is heated to the boiling point, the precipitate filtered, washed with hot water and ignited.

TABLE III

THE DETERMINATION OF METALS IN ORGANIC HALOGEN COMPOUNDS

Compound	Formula	Metal present, %		Found, %	Error
Diphenylarsyl iodide	$C_{12}H_{10}AsI$	As,	21.05	21.00	−0.05
Diphenylstibyl iodide	$C_{12}H_{10}SbI$	Sb,	30.23	30.20	− .03
Diphenylbismuthyl iodide	$C_{12}H_{10}BiI$	Bi,	42.65	42.57 (as Bi_2O_3)	− .08
				42.67 (as $BiPO_4$)	+ .02

The authors express their sincerest appreciation for the invaluable suggestions offered by Professors H. H. Willard and F. F. Blicke.

[10] Schulek and Villecz, *Z. anal. Chem.*, *76*, 81 (1929).

[11] Győry, *ibid.*, 32, 415 (1893); Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 1928, Vol. II, p. 580; Kolthoff and Furman, "Volumetric Analysis," John Wiley and Sons, Inc., New York, 1929, Vol. II, p. 464.

[12] Moser, *Z. anal. Chem.*, *45*, 19 (1906).

[13] Stahler, *Chem.-Ztg.*, 31, 615 (1907).

[14] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Company. Inc., New York, 1927, Vol. I, p. 74.

Summary

A general method has been developed for the determination of halogens in organic compounds, based upon oxidation of the substance by fuming sulfuric acid and distillation of the halogen formed. If the compound to be analyzed contains arsenic, antimony or bismuth, these metals, in addition to the halogen, may be determined in the same sample very easily.

The method of analyses requires only a short time and possesses decided advantages over the Carius and the Lemp and Broderson modification of the Pringsheim–Parr procedure.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS]

THE STEREOISOMERISM OF DIPHENYL COMPOUNDS. IV[1]

BY W. M. STANLEY AND ROGER ADAMS

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Although the evidence for the obstacle theory to explain the optical isomerism possible in certain types of substituted diphenyl compounds is increasing, much more experimental work is necessary before an entirely satisfactory analysis of this phenomenon may be expected. Previous work[1b] from this Laboratory has demonstrated that compounds having all four groups in the 2,2′,6,6′-positions the same, may be resolved into optical antipodes provided each of the two rings is unsymmetrical in itself. This is substantial evidence against the theory that interference is due merely to the relative electrostatic charges on the substituted groups. The question as to how important may be the relative size of the groups in the 2,2′,6,6′-positions requires further study. This investigation has involved a careful consideration of the probable interfering forces of such groups from x-ray data.

From x-ray data it is possible to calculate the distance between the two connecting carbon atoms in diphenyl as 1.45 Å. In the same manner and by assuming the usual angles in the benzene ring, the vertical distance between the 2,2′-carbon atoms in the benzene rings may be estimated as 2.90 Å. Also by x-ray data the relative distances between the centers of the carbon atoms in the benzene ring and of the atoms or groups attached to the benzene ring may be obtained. A question for which, at the present time, there is no experimental attack arid which, therefore, cannot be settled, is the angle at which the substituting group in a benzene ring is attached. This angle must depend upon electrostatic forces

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[1] Previous papers in this series are (a) Hyde and Adams, THIS JOURNAL, 50, 2499 (1928); (b) Moyer and Adams, *ibid.*, 51, 630 (1929); Stanley and Adams, *Rec. trav. chim.*, [4] 48, 1035 (1929).

in the molecule, and hence will be affected by the position and character of the other substituting groups present. The values which have been estimated for the distances between the centers of the carbon atoms and of the attached groups are given below.

ATOMIC DISTANCES IN Å.

Values from x-ray data for aliphatic compounds		Aromatic compounds (calcd.)	Values from x-ray data for aliphatic compounds		Aromatic compounds (calcd)
C–H	1 to 1.1	0.94 to 1.04	H-OH	1.11	
C–N (amino)	1.48	1.39	C–Cl	2.01 (calcd.)	1.89
C–C (methyl)	1.54	1.45	C–F	1.48 (calcd.)	1.39
C–I	2.2 to 2.5	2.06 to 2.35	C–COOH	1.07 (calcd.)	1.56
C–Br	2.1 to 2.4	1.97 to 2.26	C–OH	1.62 (calcd.)	1.54
H–I	1.5	....	C–NH_2	1.66 (calcd.)	1.56
H–Br	1.42	....	C–CH_3	1.84 (calcd.)	1.73
H–Cl	1.28	....	C–NO_2	2.05 (calcd.)	1.92
H–F	0.94	....	C–CH	..	1.90
H–H	0.42 to 0.48	....	C–CO	..	2.45

The first eleven atomic distances in the left-hand column determined by x-ray data were taken from the "Handbuch der Physik."[2] They represent the distances between atomic kernels, as derived from the study of aliphatic compounds. Since an aromatic carbon atom is similar in size to the carbon atoms in graphite, it is reasonable to suppose that the distances between benzene carbon atoms and the centers of the substituting groups will be somewhat smaller than in aliphatic compounds. This difference amounts to about 6%, since the diameter of an aliphatic carbon is generally given as 1.54 Å. and the diameter of an aromatic carbon atom as 1.45 Å. Therefore, 94% of the distances for the aliphatic compounds are taken as the distances involved in aromatic compounds. The distances C–Cl and C–F were calculated by extrapolation of the values determined for C–I and C–Br compared to the values determined for H–I, H–Br, H–Cl and H–F. The results obtained for C–Cl are essentially the same whether calculated through the C–I or C–Br distance. This is also true of the C–F values.

The values for C–COOH, C–NH_2, C–OH, C–CH_3, C–CH= and C–NO_2 were estimated from additional x-ray data. The length of the acetic acid molecule has been found to be 3.33 Å.[3] This represents the overall distance of a methyl group in combination with the carboxyl group. Since the sum of the radii of the two groups is taken as the distance between the centers of the two groups, the distance C–COOH is approximately 1.67 Å.

The C–NH_2 value was calculated from the distance between the kernel of a carbon atom and the kernel of a nitrogen atom in an amino group.

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[2] Grim, "Handbuch der Physik," Vol. 24, p. 539.

[3] Gibbs, J. *Chem. Soc.*, 125,2622 (1924).

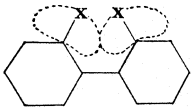
It was assumed that the increase in size of the NH_2 due to the two hydrogen atoms is less than one-half of the effective diameter of a hydrogen atom or, perhaps, 0.18 Å. The total distance C–NH_2 then becomes 1.66 Å.

For the C–OH value the experimental data necessary for calculation are very meager. Caspari,[4] after a study of amino and hydroxyl derivatives of benzene comes to the conclusion that on the basis of atomic domains, the spaces occupied by hydroxyl and amino groups cannot differ greatly from each other. Judging from the C–NH_2 value of 1.66 k., a C–OH value 1.62 Å. should be approximately correct, inasmuch as the hydroxyl ion has been shown to be somewhat smaller than an amino ion. A value for C–OH may also be calculated by a comparison of the length of octadecylbenzene[5] (24.6 k.) and octadecylphenol (25.6 Å.), which will give the effective diameter of an oxygen atom in a hydroxyl on a benzene ring as 1.0 Å. Owing to the fact that the value obtained by studying such large molecules is probably too small and that in an aliphatic compound the substituent is larger, 0.15 Å. was added to the determined value for the oxygen atom. The total value of 1.15 Å. together with the diameter of a hydrogen atom, 0.45 k., gives a final value of 1.60 Å. for the C–OH, which is essentially the same as the previously estimated value.

The distance C–CH_3 was calculated by assuming the three hydrogen atoms to increase the length of the C–C by at least two-thirds of the diameter of a hydrogen atom, or 0.30 k., the distance C–CH= by assuming the hydrogen to increase the size of the aromatic CR= group by the effective diameter of the hydrogen atom, the distance C–NO_2 by assuming the two oxygen atoms to increase the length of C–N by at least one-half the effective diameter of an oxygen atom. The distance C–CO in a quinone ring was estimated by assuming the oxygen to increase the aromatic C–C value by the effective diameter of an oxygen atom on a benzene ring.

It is interesting to note that the calculated distance between an aromatic carbon atom and substituents are of the same order as the diameters of the corresponding ions of the substituents.

The relative values given in the table should not be considered as representing merely a linear effect. The forces around a group which might interfere with the forces around another group are certainly three dimensional in character. If these forces are assumed to be effective in an area of the character of an irregular ellipsoid (see diagram), as might be expected in view of the particular linking of carbon atoms in the diphenyl molecule, the shortest distance between the 2,6- or 2′,6′-carbon atoms in diphenyl would be included in the effective areas and the table values would, therefore, have significance as far as determining the



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[4] Caspari, *Phil. Mag.*, 4, December (1927).

[5] Shearer, J. *Chem. Soc.*, **123,3152 (1923).**

relative degree of collision that occurs in the various types of substituted diphenyl compounds. It seems probable, however, that the area of the forces might vary somewhat with the character of the group, and only by experiment may this be determined.

The amount of interference caused by several combinations of 2,2′,6,6′-substituted groups has been calculated by subtracting from the sum of the distances between C–X and C–Y, the 6,6′-substituted groups, the vertical distance between the 6,6′-carbon atoms, 2.90 Å. Compounds with just two different kinds of groups in the 2,2′,6,6′-position were selected since these are by far the most readily prepared and include those already described. The calculations based on the internuclear distances previously estimated are given in the following table.

CALCULATIONS BASED ON INTERNUCLEAR DISTANCES

Groups in positions 2,2′	6.6'	Sum of internuclear distances of 2,2′-groups in Å.	Interference over 2.90 Å., vertical distance between 2,2′-carbon atoms	Groups in positions 2,2′	6,6′	Sum of internuclear distances of 2,2′-groups in Å.	Interference over 2.90 Å., vertical distance between 2,2′-carbon atoms
CH_3	CH_3	3.46	0.56	COOH	F	2.95	0.05
CH_3	NH_2	3.29	.39	F	Cl	3.28	.38
COOH	Cl	3.45	.55	F	F	2.78	− .12
COOH	CH	3.46	.56	F	OH	2.93	.03
COOH	CO	4.01	1.11	F	NH_2	2.95	.05
OH	CH	3.44	0.54	F	CO	3.91	1.01
COOH	NO_2	3.48	.58	OH	OH	3.08	0.18
COOR	Cl	3.45	.55	OH	NH_2	3.1	.20

Compounds representing the first eight combinations listed in the above table have been previously prepared and resolved into optical antipodes. None of the optically active forms of these compounds could be readily racemized. From these data it can be concluded that a difference of at least 0.39 Å. or more is sufficient to prevent practically complete rotation of the benzene nuclei into the same plane, provided this interfering effect is the only one involved.

Kenner[6] and Kuhn[7] have prepared the 2,4′-dinitro-6,6′-dicarboxydiphenyl and the 2,4,4′-trinitro-6,6′-dicarboxydiphenyl. Both of these compounds are readily racemized in alkaline solution. They are the only representatives yet prepared and resolved which have merely three substituents in the 2,2′,6,6′-positions. Those compounds with four groups present have at least two points of collision to aid in resisting racemization. Such tetrasubstituted compounds and especially those representatives which have two pairs of similar groups present in the proper positions are essentially symmetrical in regard to electrostatic or mechanical forces. In

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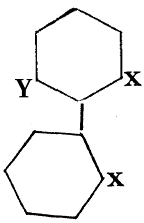
[6] Christie and Kenner, J. Chem. *Soc.*, 121,614 (1922); 470,671 (1926).

[7] Kuhn and Albrecht, Ann., 455,272 (1927); 458,221 (1927).

the trisubstituted compounds, however, there may be only one point of collision at any one instant and, at the same time, much less symmetry in the molecule. Hence the possibility is greater that a distortion of the molecule, due either to electrostatic forces or to other factors, may take place and aid racemization. In other words, the assumption is that during racemization, at the instant when the two rings move through the same plane, there may be a tendency in the trisubstituted compound for the rings to be bent toward each other on the side where the one substituting group and the hydrogen are present (see diagram). This decreases the effective interfering forces on the other side of the molecule and racemization takes place readily. It may be that such distortion is greater in 6,6′-dicarboxy compounds when the carboxyl groups are ionized, due particularly to the strongly repelling electrostatic forces of the ions.



With these assumptions it is possible to make predictions as to diphenyl compounds which might not be resolved, to others which could be resolved but which would racemize readily, and to still others which could not be racemized at all. It will be noticed from the table that in the case of the 2,2′-difluoro-6,6′-dicarboxydiphenyl, the interfering values amount only to 0.05 Å., and consequently the active forms of this compound should show a much greater tendency to racemize than the active forms of those compounds previously studied. In a communication published several years ago Kenner[8] mentioned that he intended to prepare 2,2′-difluoro-6,6′-dicarboxydiphenyl and in a recent letter (January, 1930), stated that he had already started this problem. On the other hand, a tetrafluorodiphenyl with the proper substitution to make each ring unsymmetrical in itself could not be resolved if the values mentioned have any significance, since the 2,6-fluorine atoms would fail to reach the 2′,6′-fluorine atoms by 0.12 Å. The 2,2′-difluoro-6,6′-diaminodiphenyl or 2,2′-difluoro-6,6′-dihydroxydiphenyl derivatives should be like the 2,2′-difluoro-6,6′-dicarboxydiphenyl. They would probably resolve, but would be expected to racemize readily since the o-substituted groups would interfere by 0.05 and 0.03 Å., respectively. The acetylated derivatives, however, should perhaps racemize with much greater difficulty, inasmuch as the acetyl group would probably increase the interference. Other combinations such as a 2,2′,6,6′-tetrahydroxydiphenyl or 2,2′-dihydroxy-6,6′-diaminodiphenyl, having interferences of 0.18 and 0.20 Å., respectively, would be expected to racemize with greater difficulty than either of the above-mentioned combinations, and with less difficulty than any of the first eight combinations listed in Table II. Representatives of these compounds are now being studied with a view to determine how reliable the conclusions from x-ray data may be. Of even more interest is the de-

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[8] Kenner, *Chemistry and Industry*, **46**, 218 (1927).

sirability of further study of the rather difficultly prepared $2,2',6$-trisubstituted diphenyls and their tendency to racemize. If the assumptions outlined are sound, it might be anticipated that trisubstituted compounds of all gradations of stability to racemization could readily be found. In fact, if the sum of the distances from the carbons to each of the three substituting groups and of the carbon to hydrogen is appreciably greater than twice the perpendicular distance between the α,α'-carbon atoms (2 × 2.90 Å.), no racemization should occur. If the sum is only slightly greater, the substances should racemize and if less, no resolution should be possible. Following out this plan of reasoning, it should even be possible to resolve merely a disubstituted α,α'-diphenyl provided the two groups were sufficiently large.

Slightly different methods of calculating interferences which are also based on x-ray data may be used, but the relative values are nearly the same. As a consequence the simplest method which involved the least amount of calculation was selected for discussion in this paper.

The authors wish to express here their appreciation to Dr. George L. Clark of the Chemistry Department of the University of Illinois for his assistance and advice in using the x-ray data.

Summary

A discussion is given of the expected isomerism of certain diphenyl compounds from a consideration of distances between the ring carbons and the centers of the substituting groups as deduced from x-ray data.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

SOME DERIVATIVES OF DIPHENYL ETHER

BY L. CHAS. RAIFORD, G. W. THIESSEN AND I. J. WERNERT

RECEIVED NOVEMBER 12, 1920 PUBLISHED MARCH 6, 1930

Raiford and Colbert[1] brominated 4-nitrodiphenyl ether and obtained a dibromo derivative that melted at 79°,[2] but the halogen atoms were not oriented. In the work now reported this structure was determined by two syntheses. When 4-nitrochlorobenzene was heated with the potassium salt of 2,4-dibromophenol,[3] as explained below, the ether melt-

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[1] Raiford and Colbert, THIS JOURNAL, 48, 2652 (1926)

[2] This melting point is not recorded in the published report but is given in the typed thesis on file in the University Library.

[3] The material available was not pure. It contained 62.26% of bromine instead of 63.49% calculated. It was converted into the benzoyl ester which, after several crystallizations, melted at 96° [*Ber.*, 40, 747 (1907)] and analysis for bromine indicated a pure product. The phenol obtained by hydrolysis melted at 35°. Korner [*Ann.*, 137, 205 (1866)] reported 40°, while Peratoner [*Gazz. chim. ital.*, 16, 402 (1886)] found 35–36°.

ing at 79° was obtained. In a second synthesis 4-nitrochlorobenzene was heated with the potassium salt of 2-bromophenol and the resulting ether, m. p. 82°, which must have halogen in position 2′, was subjected to the action of bromine. The dibromo ether melting at 79° was obtained in this case also, which shows that the product in question is 4-nitro-2′,4′-dibromodiphenyl ether. Attempts to obtain this product by bromination of the 4-nitro-4'-bromo derivative under the same conditions were not successful, which indicates that in the preparation of the dibromo compound by direct bromination of *p*-nitrodiphenyl ether the halogen atom that entered first must have taken position 2'.

Similar observations were made with a dinitro derivative of phenyl ether. The 2,4-dinitro-2′-bromo compound, obtained by the interaction of 2,4-dinitrochlorobenzene with the potassium salt of o-bromophenol, was converted by standing with excess of bromine and a crystal of the iodine into a dibromo derivative. The position of the second bromine atom in this product was indicated by synthesis of the compound directly from 2,4-dibromophenol. The isomeric 2,4-dinitro-4′-bromodiphenyl ether did not react with bromine under the conditions of the previous experiments. When the mixture was heated in a sealed tube at 180° for seven hours, it gave a product that melted at 140–141°, and which appeared upon analysis to be a dinitrotribromo derivative, but which was not identical with 2,4-dinitro-2′,4′,6′-tribromodiphenyl ether, m. p. 130.5°, previously reported by Raiford and Colbert.[1] It is still under consideration.

A second point of interest in this work was the behavior of some of these ethers when nitrated. 4-Nitro-4'-bromodiphenyl ether lost bromine and gave the 2,4,2′,4′-tetranitro derivative[4] first prepared by Willgerodt. When the 2′,4′-dibromo compound was nitrated, two products were isolated, but not always from the same reaction mixture.[5] One was Willgerodt's tetranitro ether, while the other gave analytical data indicating a trinitro compound in which the bromine of the starting material had been retained. It melted at 139° and was not identical with 2,4,6-trinitro-2′,4′-dibromodiphenyl ether, m. p. 163–164°, which was synthesized from picryl chloride and 2,4-dibromophenol for this comparison.

The structures of the mono and dibromo derivatives of diphenyl ether first obtained by Hoffmeister[6] and by Mailhe and Murat[7] by direct bromination of the ether have recently been determined by LeFèvre, Saunders and Turner.[8] Nevertheless, the difficulties met in this Laboratory in trying to replace the nitro radical of 4-nitro-2′,4′-dibromodiphenyl ether

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[4] Willgerodt, Ber., **13**, 887 (1880).

[5] The experiment was repeated several times but not with constant results.

[6] Hoffmeister, *Ann.*, 159, 210 (1871).

[7] Mailhe and Murat, Bull. *soc. chim.*, **11**, 328 (1912).

[8] LeFèvre, Saunders and Turner, *J. Chem. Soc.*, 1168 (1927).

with halogen by diazotizing the corresponding amino compound and subjecting the product to the Sandmeyer reaction made it necessary to study this change with simpler derivatives. Therefore, mono and dibromo derivatives of diphenyl ether were prepared in this way.

Treatment of the diazonium salt of 4-aminodiphenyl ether with cuprous bromide solution gave a 42% yield of the monobromo derivative that boiled at 295–298° at room pressure and at 143–144° at 7 mm.[10] The 4,4′-dibromo ether was obtained in a similar way. When 4-acetylaminodiphenyl ether, m. p. 128–129°,[11] in glacial acetic acid solution was treated with the theoretical quantity of bromine it gave a monobromo compound. Hydrolysis of this acetyl derivative with hydrochloric acid gave a 93% yield of the amine hydrochloride. This was diazotized and the product converted into the perbromide by a slight modification of the method of Biilow and Schmachtenberg.[12] Decomposition of this product by refluxing it with glacial acetic acid for thirty minutes gave a 73% yield of a dibromo derivative identical with that obtained by direct bromination of diphenyl ether.

The behavior just noted is in marked contrast to that observed when 4-amino-2′,4′-dibromodiphenyl ether was used. In this case the diazonium salt did not give a clear solution, and treatment of the suspension with cuprous bromide gave a quantity of material too small to purify and identify. Treatment of another portion with a potassium bromide solution of bromine gave a low yield of yellow solid that appeared to be perbromide. Boiling this with acetic acid gave a very small amount of dark oil which could not be identified.

When 4-amino-2′,4′-dichlorodiphenyl ether, prepared from 4-nitrochlorobenzene and 2,4-dichlorophenol by the general method, was diazotized, a clear solution of the diazonium salt was obtained. Treatment of this with cuprous chloride gave but 17% of the required trichloro ether, which indicates the extent to which activity is decreased by the presence of the second halogen atom.

Experimental Part

The diphenyl ethers studied here were prepared, in general, as follows. When only one nitro radical was present in the halogenated benzene used, this was mixed with a water solution containing one-fourth more than

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[9] This did not give a clear solution but a pale yellow suspension.

[10] Suter [THIS JOURNAL, **51**, 2585 (1929)] recorded 160–165° at 14 mm. for *p*-bromodiphenyl ether prepared by direct bromination.

[11] Mailhe [*Compt. rend.*, **154**, 1241 (1921)] reported 99°, but Haeussermann and Teichmann [*Ber.*, 29, 1447 (1896)] had previously recorded 127". Neither author analyzed his product, but the discrepancy may be explained by the possibility that Mailhe had the diacetyl derivative, for Sudborough [*J. Chem. Soc.*, *79*, 536 (1901)] found that the monoacetyl compound has the higher melting point of the two.

[12] Biilow and Schmachtenberg, *Ber.*, **41**, 2607 (1908).

TABLE IA

DERIVATIVES OF DIPHENYL ETHER

	Compound	Solvent	Crystal form	Yield, %
1	4-Acetylamino-4-bromo	EtOH	Colorless plates	Nearly quant.
2	4-Nitro-2'-bromo	EtOH + AcOH[a]	Nearly colorless needles	44
3	4-Nitro-2',4'-dibromo	EtOH	Pale brown needles	83
4	4-Amino-2',4'-dibromo	......	Oil	77
5	4-Acetylamino-2',4'-dibromo	Dil. AcOH	Nearly colorless needles	Nearly quantitative
6	2,4-Dinitro-2'-bromo	EtOH + AcOH	Pale yellow needles	82
7	2,4-Dinitro-2',4'-dibromo	EtOH	Yellow flakes	Nearly quant.
8	4-Nitro-2',4'-dichloro	EtOH + AcOH	Cream-colored needles	79
9	4-Amino-2',4'-dichloro	EtOH	Brown diamond-shaped crystals	60
10	4-Acetylamino-2',4'-dichloro	EtOH	Colorless needles	Nearly quantitative
11	4,2',4'-Trichloro	EtOH	Colorless needles	17
12	2,4-Dinitro-2',4'-dichloro	EtOH + AcOH	Pale yellow plates	78
13	2,4,6-Trinitro-2',4'-dibromo	EtOH + AcOH	Short yellow needles	85
14	?-Trinitro-2',4'-dibromo	AcOH + toluene	Yellow flakes	Nearly quant.

[a] Approximately 2 volumes of alcohol and 1 volume of glacial acetic acid.

TABLE IB

DERIVATIVES OF DIPHENYL ETHER

				Analyses					
	Formula	M. p., °C.	Subs., g.	0.1 *N* acid, *cc.*	Nitrogen, % Calcd.	Nitrogen, % Found	0.1 A' AgNO$_3$, *cc*, or wt. of Ag hal., g.	Halogen, % Calcd.	Halogen, % Found
1	$C_{14}H_{12}O_2NBr$	157	0.2977	...	..	..	0.1815	26.12	26.11
2	$C_{12}H_8O_3NBr$	82	.4111	13.65	4.76	4.59	.....	...	...
			.2939	...	..	..	10.18	27.21	27.27
3	$C_{12}H_7O_3NBr_2$	79	.2238	5.89	3.75	3.80	.....	...	...
			.3317	...	..	..	17.93	42.89	42.48
4	$C_{12}H_9ONBr_2$	Oil, 225–230° (10 mm.)	.2356	...	..	..	0.2580	46.61	46.60
5	$C_{14}H_{11}O_2NBr_2$	158	.2023	...	..	..	0.1971	41.55	41.47
6	$C_{12}H_7O_5N_2Br$	88–89	.5180	30.52	8.25	8.25	.....	...	...
			.3472	...	..	..	10.61	23.59	23.99
7	$C_{12}H_6O_5N_2Br_2$	131	.2304	11.22	6.69	6.83	.....	...	...
			.2019	...	..	..	9.87	38.27	38.24
8	$C_{12}H_7O_3NCl_2$	71	.2524	...	..	..	0.2545	25.08	24.96
9	$C_{12}H_9ONCl_2$	62	.2512	...	..	..	,2843	27.95	27.98
10	$C_{14}H_{11}O_2NCl_2$	144	.2783	...	..	..	.2707	2'3.97	24.07
11	$C_{12}H_7OCl_3$	51	.2056	...	..	..	.3216	38.93	38.72
12	$C_{12}H_6O_5N_2Cl_2$	118	.2472	15.02	8.51	8.51	.....	...	...
			.2684	...	..	..	16.56	21.58	21.52
13	$C_{12}H_5O_7N_3Br_2$	163–164	.3116	20.0	9.07	9.04	.....	...	...
			.3019	...	..	..	13.25	34.55	35.00
14	$C_{12}H_5O_7N_3Br_2$	139	.2294	15.66	9.07	9.56	.....	...	...
			.2823	...	..	..	12.36 .	34.55	34.40

the theoretical amount of the potassium salt of the required phenol, the mixture evaporated to dryness and then heated on an oil-bath for three hours at 150–170°. Unchanged nitrobenzene derivative was then removed by distillation with steam, and the non-volatile residue (ether) purified in a suitable manner. When two or more nitro radicals were present in the starting material, the "wet method" described by Raiford and Colbert[13] gave best results. With the exceptions noted above, other derivatives were prepared by standard methods that will not be described here. The yields, general properties and analytical data for these substances are given in the tables.

Summary

1. When 4-nitrodiphenyl ether is brominated as here described, the halogen atoms enter positions 2' and 4' only, although excess of bromine may be present. Position 2' is probably attacked first.

2. Nitration of 4-nitro-2',4'-dibromodiphenyl ether gave two products: the 2,4,2',4'-tetranitro compound, and a trinitro derivative in which all bromine is retained.

3. Increase in the number of substituents seems to interfere with diazotization of an aminophenyl ether.

4. Several new derivatives of diphenyl ether have been synthesized and their structures established.

IOWA CITY, IOWA

[CONTRIBUTION NO. 185 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

A STUDY OF THE PENTOSE AND URONIC ACID CONTENT OF ORANGE ALBEDO, AND AN ARABINO-GALACTURONIC ACID DERIVED FROM ORANGE PECTIN

BY JOHN R. BOWMAN AND RONALD B. MCKINNIS

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I. Introduction

This work was undertaken to determine the relative amounts of combined pentose and uronic acid in orange pectin, as it occurs in the albedo of commercial ripe oranges, and subsequently to see if the relation of these substances is similar to that in apple pectin.

Apple tissue has been found previously to contain no free pentose and the pectin to contain no combined pentose.[1] The furfural obtained on distillation with hydrochloric acid was quantitatively attributed' to the galacturonic acid part of the pectin, arabinose being an intermediate stage in the decomposition.

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[13] Ref. 1, p. 2659.

[1] **Ronald B. McKinnis, THIS JOURNAL, 50, 1911 (1928).**

The present analytical procedure has a decided advantage in that it does not involve the use of empirical constants. However, the results justify the conclusions arrived at by the use of the former method.[1] Dore[2] has used a similar method, but did not apply it in the same manner.

II. The Simultaneous Determination of Pentose and Uronic Acid

A. Theoretical.—As is well known, pentoses split off water on boiling with dilute acids, giving furfural. This distils and can be precipitated almost quantitatively with phloroglucinol. The maximum yield of furfural is not obtained, but the results are practically constant and therefore comparable. Uronic acids first split off carbon dioxide to form a pentose; then the pentose splits off water to form furfural. A 100% yield of carbon dioxide and about 34% of the possible theoretical yield of furfural are obtained from combined galacturonic acid.

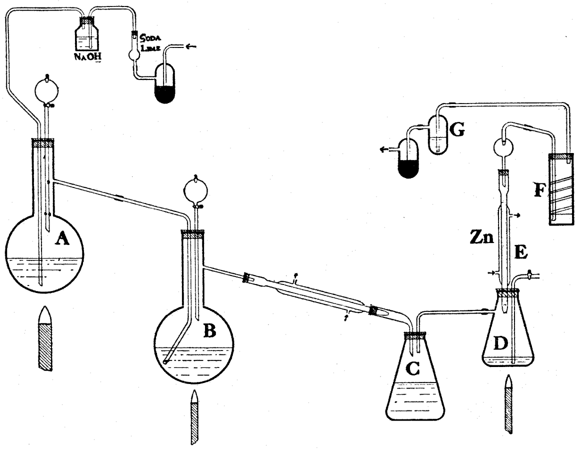

Fig. 1.

Certain α-hydroxy acids under the action of mineral acids break down into aldehydes with the elimination of formic acid, which would decompose forming carbon monoxide, but in this case no carbon monoxide could be detected in a typical experiment. This result, together with the good yields of carbon dioxide obtained from digalacturonic acid and barium galacturonate, indicates that the formic acid type of decomposition does not take place to any appreciable extent under the conditions of the experiment.

B. Apparatus and Procedure.—Most of the details of the distillation train are evident from Fig. 1. The steam generator, A, contains a trace of sodium hydroxide, and the steam inlet tube to the main reaction flask, B, is bent so as to give the contents a swirling motion. The furfural distillate is collected in C at 0°. The condenser, E, is filled with fine mossy zinc kept moist by refluxing from D to prevent any hydrochloric

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[2] W. H. Dore, *ibid.*, 48, 232 (1926).

acid from distilling into the barium hydroxide in F and G. G remained clear throughout the work. A slow current of air previously freed of carbon dioxide is drawn from A to G. At each end of the apparatus is a small trap filled with mercury.

The sample and 200 cc. of exactly 12% hydrochloric acid are placed in Flask B. The carbon dioxide is swept out by applying suction to D, and the water in D is brought to a boil. The suction is now started at G, the reaction flask heated, steam blown through and the flame adjusted so that the mixture remains at constant volume. The receiver, C, is fitted with a device (not shown in the figure) which allows sampling of the distillate without an influx of carbon dioxide. A glass tube inserted obliquely in the stopper and closed with rubber tubing and a clamp allows sampling the distillate without an influx of carbon dioxide. The distillation is stopped half an hour after a practically colorless test is obtained with aniline acetate paper. This usually requires three and one-half to four hours, but a faint pink color persists even after six hours.

Carbon dioxide is determined by titration of the barium hydroxide with **0.1** *N* hydrochloric acid, both before and after the distillation. Furfural is determined as the phloroglucide, without washing with alcohol, the difference being insignificant.

C. Results Obtained on Digalacturonic Acid.—The digalacturonic acid was prepared from apple pectin by the procedure already reported.[1] The results, Table I, show that the actual yields of carbon dioxide and furfural are 100 and 34%, respectively, of the theoretical.

TABLE I

FURFURAL AND CARBON DIOXIDE YIELDS FROM DIGALACTURONIC ACID

Sample, g.	CO_2, g.	Yield, %	Furfural, g.	Yield, %	$\frac{\text{Moles furfural}}{\text{Moles } CO_2}$
0.3012	0.0719	100	0.0541	34.6	0.34
.3025	.0716	99.5	.0526	33.5	.33

D. Results Obtained on Orange Albedo.—Ripe commercial oranges were used throughout the work. The pulp and flavedo were removed and the albedo rinsed in cold water, then squeezed out and stored in absolute alcohol. It is interesting that the alcohol extracted no pentoses. Just before use it was washed in fresh alcohol, dried in a current of air at room temperature and crushed to a powder. Table II shows the results with this material.

TABLE II

FURFURAL AND CARBON DIOXIDE YIELDS FROM ORANGE ALBEDO

Sample, g.	CO_2, g.	Furfural, g.	$\frac{\text{Moles furfural}}{\text{Moles } CO_2}$
7.02	0.0292	0.0438	0.68
8.21	.0315	.0433	.64
8.45	.0390	.0563	.66

Comparison of this ratio with that of Table I shows that there was twice as much furfural as carbon dioxide in the orange albedo. Since uronic acids give one mole each of carbon dioxide and furfural, and pentoses give one of furfural only, this result clearly indicates an equal proportion of combined pentose and uronic acid in the orange albedo.

III. Arabino-galacturonic Acid from Orange Albedo

A. Preparation.—Five hundred grams of prepared orange albedo was covered with 1% sodium hydroxide solution and heated for an hour with frequent stirring. The extract was made slightly acid with hydrochloric acid, raised to the boiling point and the crude arabino-galacturonic acid filtered off. The precipitate was then redissolved in a liter of 1% sodium hydroxide solution, allowed to stand for a few moments, then neutralized, warmed and filtered off again. The process was repeated through at least seven reprecipitations, decolorizing carbon being added to the alkaline solution the last few times and filtered off before neutralization. After the last precipitation, the precipitate was washed with hot water until no longer acid, then dried in a vacuum at 35 to 40° and ground. The yield of 1 g. was less than 10%, calculated on the basis of carbon dioxide determinations on the original albedo.

B. General Properties.—The compound is light tan to buff in color, practically odorless and tasteless, and has no melting point, decomposition beginning at rather low temperatures. It is insoluble in water and all the common organic solvents, but dissolves easily in dilute aqueous alkalies. The alkali is almost completely removed by dialysis, giving a sol which is immediately coagulated by small quantities of inorganic acids and salts. The action on ammoniacal silver and Fehling's solution is very slow, indicating that the aldehyde groups are not active. Definite salts of barium, potassium or sodium could not be made.

IV. Evidence for the Constitution of Arabino-galacturonic Acid

A. Combined Pentose and Uronic Acid Determination.—When the acid was first prepared, it was expected to be digalacturonic acid, but Table III shows that such was not the case. The compound gave the same ratio as did the albedo, showing that it also contains equal amounts of combined pentose and uronic acid.

TABLE III

FURFURAL AND CARBON DIOXIDE YIELDS FROM ARABINO-GALACTURONIC ACID

Sample, g.	CO_2, g.	Yield, %	Furfural, g.	Yield, %	$\frac{\text{Moles furfural}}{\text{Moles } CO_2}$
0.2983	0.0402	99.7	0.0533	30.3	0.61
.3113	.0419	99.6	.0625	34.1	.68
.0155	.0021	100.9	.0031	34.0	.68

B. Hydrolysis of Arabino-galacturonic Acid.—Hydrolysis was accomplished by a method similar to that used by Ehrlich and Sommerfeld[3] for the preparation of galacturonic acid from digalacturonic acid.

Three or four grams of arabino-galacturonic acid was refluxed for seventeen and one-half hours with 2% sulfuric acid and decolorized with charcoal.

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[3] F. Ehrlich and R. V. Sommerfeld, *Biochem. Z.*, 168, 263 (1926).

A simultaneous determination of the furfural and carbon dioxide evolved during the hydrolysis revealed the fact that furfural was evolved but only a trace of carbon dioxide. This showed that the pentose was partially broken down, but that the uronic acid was almost untouched by the treatment.

C. Separation and Identification of Galacturonic Acid.—The hydrolyzed solution was exactly neutralized with barium hydroxide, filtered, concentrated to 100 cc. and poured into three times its volume of alcohol. The precipitate was filtered off, washed with alcohol, then redissolved in water and reprecipitated with alcohol three times. The product, dried in a vacuum and ground, was a straw-colored powder. The yield of about 0.2 g. gave 27.5% barium, compared with 26.3% calculated for $Ba(C_6H_9O_7)_2$.

The carbon dioxide and furfural determinations given in Table IV show that the compound was barium galacturonate.

TABLE IV

FURFURAL AND CARBON DIOXIDE YIELDS FROM BARIUM GALACTURONATE

Sample, g.	CO_2, g.	Yield, %	Furfural, g.	Yield, %
0.1325	0.0214	96	0.0171	35
.1941	.0310	95	.0244	34

Neutralization of the barium salt with sulfuric acid gave a solution of galacturonic acid. Oxidation with bromine at room temperature for four days gave 60.5% of the theoretical yield of mucic acid, and oxidation for nine days at room temperature and then for seven hours at 35–40° gave a 69.1% yield. Ehrlich and Sommerfeld[3] report 67.9% when at room temperature for seven days. The optical rotation of the galacturonic acid solution, $[\alpha]_D^{22}$ +53.6, compares favorably with Ehrlich's value, $[\alpha]_D^{20}$ +53.4. These results indicate that the uronic acid left after the combined pentose had been split off with the 2% sulfuric acid is galacturonic acid.

D. Separation and Identification of Arabinose.—A slight excess of barium hydroxide was added to another portion of the hydrolyzed material with sufficient alcohol to precipitate the organic acids. Barium was removed with sulfuric acid. Crystallization was impossible, but a hydrazone was prepared which melted at 204°. The reported value for 1-arabinose diphenylhydrazone is 203–205". The hydrazone from Eastman's *l*-arabinose melted at 204°. Only a small amount was available for a carbon dioxide and furfural determination, but a 27% yield of furfural was obtained and no carbon dioxide.

These results show that the pentose is 1-arabinose and that the pentose-uronic acid is arabina-galacturonic acid or a polymer of it.

V. Discussion of Results

Ratios of moles of carbon dioxide and furfural obtained indicate the existence of two acid compounds in pectin, one giving half as much carbon dioxide as the other. The yield of carbon dioxide is 100% and of furfural 34% for galacturonic acid as determined on barium galacturonate. These figures when applied to the two acids indicate that one may be digalacturonic acid and the other arabino-galacturonic acid. Further proof of the composition of arabino-galacturonic acid is given by the production of furfural without carbon dioxide by means of weak acids. Galacturonic acid remains, and was identified by its barium salt, optical rotation and yields of furfural, carbon dioxide and mucic acid. Arabinose was isolated from the same solution and identified as 1-arabinose diphenylhydrazone.

It was previously found that apple tissue gives the same ratio as does digalacturonic acid isolated from it, but this work shows that orange albedo gives the same ratio as arabino-galacturonic acid. Since no free arabinose is present, it can be concluded that the pectin in orange albedo contains groups giving furfural and carbon dioxide in the same ratio as in arabino-galacturonic acid, which probably is the real nucleus to which the methyl groups, etc., are attached. A polymer or association compound of either of the acids is possible, since our work does not indicate the molecular weight.

The absence of pentoses in the alcoholic washings of the albedo, and the ratio of the moles of furfural to carbon dioxide in the albedo and in the arabino-galacturonic acid show that free pentoses are not present in orange albedo. There is little doubt that the oxidation of galactose to galacturonic acid and subsequent decarboxylation forms arabinose in nature, but it is still doubtful whether free arabinose ever occurs naturally.

The arabino-galacturonic acid could readily be formed from the digalacturonic acid by mere splitting off of one mole of carbon dioxide. Further changes need not necessarily be like the hydrolysis with 2% sulfuric acid.

Smolenski and Wlostowska[4] have studied the hydrolysis products of beet pectin. They found araban, galactan and a digalacturonate as the main products, but no proof was given that the araban or galactan or both were not formed from the galacturonate during hydrolysis.

Since one acid may be derived from the other, it is possible that both occur in some pectins. Nanji, Paton and Ling[5] obtained 20% of furfural and 17.64% of carbon dioxide from pectic acid. A mixture of 40% of digalacturonic acid and 60% of arabino-galacturonic acid would give 19.2% of furfural and 17.56% carbon dioxide. The present results do not confirm the hexa ring formula of Nanji, Paton and Ling.[5] No reliable data for galactose in pectin is available, so this point is still in doubt.

Ehrlich and Schubert[6] obtained 0.0958 g. of furfural from 0.4998 g.

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[4] K. Smolenski and W. Wlostowska, *Roczniki Chem.*, 7, 591 (1927), C. A., **22,** 4109 (1928).

[5] D. R. Nanji, F. J. Paton and A. R. Ling, *J. Soc. Chem. Ind.*, **44,** 253T (1925).

[6] F. Ehrlich and F. Schubert, *Biochem. Z.*, 169, 13 (1926).

of pectic acid and 0.1605 g. of carbon dioxide from 1.2364 g. of the same material. From these figures the ratio is found to be 0.676, closely agreeing with the ratio found for arabino-galacturonic acid.

Norris and Schryver[7] obtained 20.32% of furfural from pectinogen extracted by ammonium oxalate, and found 50.9% of galactose as determined by mucic acid. Mucic acid, however, is also derived from galacturonic acid; arabino-galacturonic acid would give a theoretical value of 52.3% for such a determination, and their figures agree with this value within the limits of experimental error.

The present results and the results of others indicate that pectin can vary in composition, and that its hydrolysis products may be the cause of the confusion in regard to its composition.

The work seems promising and is being continued with the hope that order may be brought out of the present confusion.

The authors wish to express their appreciation to Dr. C. G. King for his suggestions and interest in the work.

VI. Summary

1. A method has been found for simultaneously determining the relative number of furfural yielding and uronic acid components, and has been used to study the composition of orange albedo pectin and its nucleus.

2. An arabino-galacturonic acid has been isolated from orange albedo and shown to yield two moles of furfural to one of carbon dioxide, as did the original orange albedo.

3. Orange albedo has been shown to contain no free pentose.

4. Hydrolysis of arabino-galacturonic acid with a dilute acid splits off only the arabinose, which is further hydrolyzed to form furfural. With stronger acids the carboxyl of the galacturonic acid is also split off to form more arabinose, which also is hydrolyzed to furfural. Arabinose and galacturonic acid were isolated from the products of dilute acid hydrolysis. These facts and the furfural and carbon dioxide yields establish the composition of the acid nucleus of orange albedo pectin.

5. Digalacturonic acid and arabino-galacturonic acid were probably successive steps in the production of arabinose.

6. Arabino-galacturonic acid or a polymer is probably the nuclear unit of orange albedo pectin.

7. Since digalacturonic acid has been found in apple pectin, it is probable that some pectins contain both digalacturonic acid and arabino-galacturonic acid in varying proportions. The present results and the results of others indicate that pectin varies in composition and that its hydrolysis products cause the confusion in regard to its composition.

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[7] F. W. Norris and S. B. Schryver, *Biochem. J.*, 19, 676 (1925).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

AMMONO FURALDEHYDES

BY HAROLD H. STRAIN

RECEIVED NOVEMBER 12, 1929 PUBLISHED MARCH 6, 1930

Introduction

Because extensive investigations have shown that furaldehyde very closely resembles the common aromatic aldehydes in its chemical properties, a study of the reaction of furaldehyde with ammonia was undertaken with the hope of obtaining a series of compounds analogous to those obtained by the reaction of benzaldehyde with ammonia. Thus furaldehyde and ammonia should form hydrofuramide

$$3C_4H_3OCH{=}O + 2NH_3 = (C_4H_3OCH{=})_3N_2 + 3H_2O$$

just as benzaldehyde has been found to react with ammonia to form hydrobenzamide.[1] The hydrofuramide should then react with liquid ammonia to form furylidene-imine which is analogous to benzylidene-imine.[1]

$$(C_4H_3OCH{=})_3N_2 + NH_3 = 3C_4H_3OCH{=}NH$$

Hydrofuramide and furylidene-imine may also be regarded as aldehydes of an ammonia system of compounds as postulated by Franklin and his co-workers.[1,2] These ammono furaldehydes should therefore undergo the reactions characteristic of the ammono aldehydes such as condensation, nitridation, etc.

As a matter of fact several of the reactions mentioned above were demonstrated. However, the ammono furaldehydes proved to be much more reactive and much less stable than the corresponding ammono benzaldehydes. This reactivity, marked by ease of condensation, prevented the formation of furylidene-imine from hydrofuramide, as will be described later. As a result, only the reactions of hydrofuramide could be studied.

The formation of hydrofuramide from furaldehyde and aqueous ammonia has long been known.[3]

When hydrofuramide is treated with liquid ammonia under conditions which should ammonate it to furylidene-imine, a condensation takes place which results in the formation of furine, trifuryldihydro-imidazole. This reaction is similar to the condensation of hydrobenzamide to amarine which workers in this Laboratory consider to be analogous to the benzoin condensation followed by a Cannizzaro reaction.[4]

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[1] Strain, THIS JOURNAL, 49, 1558 (1927).

[2] Franklin, Am. *Chem.* J., 47, 285 (1912); THIS JOURNAL, 46, 2137 (1924).

[3] Fownes, *Ann.*, 54, 55 (1844); Schiff, Ber., 10, 1188 (1877).

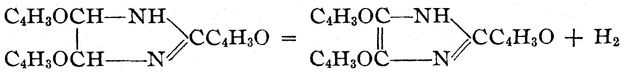
[4] Strain, Ref. I, p. 1565.

The formation of furine from hydrofuramide has also been accomplished by heating hydrofuramide with aqueous alkali.[3] The same reaction takes place quantitatively in liquid ammonia, so that very pure furine may be obtained by simply dissolving hydrofuramide in liquid ammonia and then evaporating or concentrating the solvent until crystallization occurs.

Attempts to nitridize furine with a solution of iodine in ammonia[5] to compounds analogous to those formed by the nitridation of hydrobenzamide such as lophine, cyaphenine, benzonitrile and benzamidine,[1] resulted in the formation of tar.

Similarly, attempts to convert furine into an iso-furine, just as amarine is converted into an iso-amarine, likewise met with failure.

When furine is treated with an excess of potassium amide in liquid ammonia, hydrogen is liberated. However, the quantity of hydrogen is much less than that required by the reaction



I II

In addition it was impossible to isolate the furyl compound corresponding to lophine (Formula II).[6]

Experimental

Preparation of Hydrofuramide.—Freshly distilled furaldehyde was permitted to stand for several days with an excess of concentrated aqueous ammonia, when the crystals of hydrofuramide which had formed were filtered off and recrystallized from alcohol.

Preparation of Furine.—Hydrofuramide, which is only slightly soluble in liquid ammonia at room temperature, dissolves in the course of an hour or so forming furine which is very soluble. The speed of this reaction is greatly increased by the addition of very small quantities of potassium amide. Long thin crystals of the furine thus pre-

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[5] Although we are wont to explain the reactions of a solution of iodine in liquid ammonia on the basis of the formation of ammono hypoiodous acid, there is no direct evidence that such an acid exists. Bergstrom, THIS JOURNAL, **48**, 2319 (1926).

[6] The writer has found that amarine, triphenyldihydro-imidazole, reacts with a solution of potassium amide in liquid ammonia to form hydrogen and lophine, triphenylimidazole. The analogous oxidation of many organic compounds by fused alkalies with the simultaneous evolution of hydrogen has long been known. More recently, Fry, Schulze and Weitkamp [*ibid.*, **46**, 2268 (1924)] have proposed that the reaction is caused by sodium hydroxide which has undergone acidic dissociation.

$$NaOH = NaO^- + H^+$$

The analogous dissociation of potassium amide is illustrated by the following reactions.

$$KNH_2 = KNH^- + H^+$$
$$KNH^- = KN' + H^+$$

Whether such a dissociation takes place in liquid ammonia solution or not is problematical. Solutions of hydrogen chloride in liquid ammonia do not cause the evolution of hydrogen from the hydramides.

pared are obtained by cooling the concentrated solution to −35°. These crystals melt at 117° and when mixed with crystals of furine prepared by boiling hydrofuramide with aqueous potassium hydroxide the mixture melts at 117°. The completeness of the reaction just described is attested by the fact that the residue does not give rise to the red color characteristic of furaldehyde and hydrofuramide when treated with aniline acetate.

Attempts to **Ammonate** Hydrofuramide to **Furylidene-imine.**—A suspension of hydrofuramide in liquid ammonia was treated with an excess of ammonium chloride (or ammonium bromide) while the temperature was maintained at −35° for several hours when it was found that the hydrofuramide failed to dissolve at an appreciable rate. By carrying out the reaction at 0° or at room temperature the hydrofuramide dissolved very slowly, indicating its conversion into furylidene-imine or furine. In spite of the fact that large quantities of furine were isolated from the reaction mixture, some furylidene-imine must also have been formed, as evidenced by the formation of furaldehyde when the reaction mixture was treated with aqueous acid. It was impossible to separate the furylidene-imine by crystallization from liquid ammonia.

Attempts to **Nitridize** Furine and **Hydrofuramide.**—A suspension of hydrofuramide or a solution of furine in liquid ammonia was cooled to −35° and treated with an excess of iodine. The ammonia was then allowed to boil very slowly at −33° until all the iodine had dissolved. In every experiment brown decomposition products which could not be crystallized were obtained. In many nitridations a few crystals separated from the solution. From 12 g. of furine less than 0.09 g. of crystals were obtained. They were recrystallized from glacial acetic acid and found to melt at 239° uncorr. but could not be identified.

Reaction of Furine and Potassium **Amide.**—The furine was treated with an excess of potassium amide (more than 1 mole) in liquid ammonia solution, when a very vigorous reaction took place accompanied by the evolution of heat and gas and by the production of red and brown colors. The gas which was collected over water in an eudiometer tube proved to be hydrogen.[7] No pure compounds could be isolated from the reaction mixture. The results of several experiments are tabulated below (Table I).[8]

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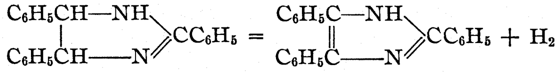
[7] For method of collecting gas see Bergstrom, THIS JOURNAL, 47, 2320 (1925).

[8] In reporting the reaction of an excess of potassium amide and amarine the writer failed to include any of the experimental results [Strain, *ibid.*, 49, 1564 (1927)]. They are included here because they illustrate the difference in reactivity of the corresponding benzylidene and furylidene compounds. The experimental procedure was the same as that described above for furine.

Expt.	Amarine, g.	Vol. of H (N. T. P.), cc.	Calcd.	% of calcd.
I	0.40	29.2	30.1	97.0
II	.30	21.4	22.6	94.7

In Expt. II 0.27 g. of lophine was recovered, indicating that the following reaction takes place almost quantitatively.



Salicylhydramide was found to react with potassium amide with the evolution of hydrogen. To effect this reaction a very large excess of potassium amide was necessary (4.5 moles). At the same time a deep blue color was produced. Although two-thirds of the hydrogen was liberated at the end of the first hour, five hours were required for its complete evolution. Two experiments using 1.5-g. portions of salicylhydramide each of which should have liberated 97.1 cc. of hydrogen (N. T. P.) resulted in the production of 89.8 and 72.5 cc. of hydrogen.

TABLE I

EXPERIMENTAL RESULTS

Expt.	Purine, g.	Vol. of H (N. T. P.), cc.	Calcd.	% of calcd.
I	0.268	13	22.4	58
II	0.500	26	41.8	62
III	1.070	43	89.4	48

Furine Nitrate.—Transparent crystals of furine nitrate prepared for the purpose of identifying furine were found to melt at 94° instead of at 154° as previously recorded.[9] After standing for two years, the crystals which had become opaque no longer melted at 94° but decomposed at 180–182°. That the change in appearance which had already been noted[10] was not due to oxidation or to the loss of water of crystallization was proved by analysis. It was then found possible to recrystallize the nitrate, when crystals melting at 94° were obtained. As these crystals were heated above their melting point they became solid again and finally decomposed at 182°. Crystals obtained from an alcohol–ether solution on the other hand decomposed at 182° without previous melting. Whether these two modifications represent dimers or whether they are the result of some more profound change in the molecule such as occurs in amarine was not determined.

The writer wishes to express publicly his appreciation of the many helpful suggestions received from Dr. E. C. Franklin.

Summary

A study of the reaction of furaldehyde and ammonia has shown that furaldehydes of the ammonia system of compounds are formed. These ammono furaldehydes are much less stable than the corresponding ammono benzaldehydes, although they do undergo many reactions characteristic of the latter.

Furine nitrate has been shown to exist in two crystalline modifications.

The reaction of potassium amide and some aromatic ammono aldehydes dissolved in liquid ammonia has been described.

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[9] Delépine, Bull. *soc. chim.*, [3] 19, 175 (1888).

[10] Stenhouse, ***Ann.***, 74,283 (1850).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE RATE OF COUPLING OF DIAZONIUW SALTS WITH PHENOLS IN BUFFER SOLUTIONS

BY J. B. CONANT AND W. D. PETERSON

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In the coupling of diazonium salts with phenols the acidity of the solution is usually regulated by the addition of the salt of a weak acid; sodium acetate, sodium bicarbonate and sodium carbonate are thus commonly employed in the manufacture of azo dyes. In order for the reaction to proceed rapidly the acidity must be kept below a certain value; this value depends on the nature of the diazonium salt and the phenol. A great mass of qualitative information of this sort suggests that the rate of the coupling reaction is a function of the hydrogen-ion activity of the solution. Although many preparative and analytical procedures are practically based on such an assumption, the point never seems to have been tested by actual measurements. The previous work on the rate of coupling of diazonium salts[1] was carried out before the advent of the modern methods of preparing and studying buffer solutions; the results are, therefore, difficult to interpret and throw but little light on the role played by the hydrogen ion (or hydroxyl ion). We have now carried out a series of measurements of the rate of coupling of five diazotized amines with five phenols and naphthols in buffer solutions of known acidity. The results show that the reaction is remarkably free from complications and that the rate is a simple function of the hydrogen-ion activity of the buffer solution employed. As a result it becomes possible to reduce to simple equations a description of the coupling reaction of a number of substances under a variety of conditions.

Experimental Procedure

The course of the coupling reaction was followed colorimetrically, the extent of the reaction being determined by comparison with the color of an identical mixture in which the reaction was complete. The acidity of the solution was controlled by heavily buffering the reaction mixture. The concentration of buffering salt was of the order of tenth molar while the maximum concentration of the reactants was thousandth molar; the change in acidity of the solution during the reaction was thus negligible. The ionic strength of all the buffersolutions was 0.24; to obtain this value potassium chloride was added in some cases. The composition of the buffers is given in Table I. The PH values were determined by the usual electrometric method using a Clark rocking electrode and were repeatedly checked.

Purification of Material.—The amines which were employed were

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[1] Goldschmidt, *Ber.*, **30**, 670, 2075 (1897); **33**, 893 (1900); **35**, 3534 (1902); Veley, *J. Chem. Soc.*, **95**, 1186 (1909).

TABLE I

BUFFER SOLUTIONS OF CONSTANT TONIC STRENGTH ($\mu = 0.24$)

Buffer	Constituent	Fraction	Constituent	Fraction	KCl per liter, g.	P_H
Acetate I	0.50 *M* NaAc	0.48	0.52 *M* HAc	0.52	None	4.50
Acetate II	.10 M NaAc	.50	.10 M HAc	.50	14.2	4.50
Acetate III	.30 M NaAc	.80	.30 *M* HAc	.20	None	5.27
Phthalate II	.10 M $C_8H_4O_4HK$	.65	.10 *M* NaOH	.35	7.85	4.94
Phosphate I	.20 *M* Na_2HPO_4	.10	.20 *M* KH_2PO_4	.90	None	5.80
Phosphate II	.15 *M* Na_2HPO_4	.30	.15 *M* KH_2PO_4	.70	None	6.30
Phosphate III	.12 *M* Na_2HPO_4	.50	.12 M KH_2PO_4	.50	None	6.73
Phosphate IV	10 M Na_2HPO_4	.70	.10 *M* KH_2PO_4	.30	None	7.08
Borate I	.10 *M* Borate	60	10 *M* HCl	.40	13.34	8.17
Borate II	.10 M Borate	1.00			10.37	9.15

sulfanilic acid, *p*-bromo-aniline, aniline, *p*-toluidine and o-anisidine; their purification presents no special problems and need not be described. The problem of purifying the sulfonated naphthols, on the other hand, is one of extreme difficulty because there are no simple criteria of purity such as boiling point or melting point. We wish to express our indebtedness in this connection to Dr. Hitch of the Jackson Laboratory of the du Pont Company for his assistance in supplying us with materials and suggesting methods of analysis; without his help we should not have been able to prepare the materials used in this research. Information in regard to the purification and analysis of the sulfonated naphthols is given below.

Sodium 1-naphthol-4-sulfonate (N and W Salt).—The zinc salt was recrystallized three times and converted into the sodium salt with sodium carbonate. Tests showed it to be free from naphthionic acid. The analysis by titration[2] with diazotized *p*-bromo-aniline and p-nitro-aniline gave values of 97.4 to 96.6% purity for the dry salt (dried over phosphorus pentoxide in *vacuo).*

Disodium 1-Naphthol-3,8-disulfonate (Epsilon Salt).—The sodium salt was recrystallized four times from hot water and dried *in vacuo* over sulfuric acid for three weeks. The test for nitrogen by means of a potassium fusion was negative. Titration with benzene diazonium chloride showed a purity of 90.2 to 91.2%.

Disodium 2-Naphthol-3,6-disulfonate (R salt).—We are indebted to Dr. Hitch of the du Pont Company for a purified sample of this material which contained no G salt or Schaeffer's salt. By diazometric titration it was found to be 76.0 to 77.6% pure.

Disodium 2-Naphthol-6,8-disulfonate (G salt).—A good grade of commercial material was extracted with 80% alcohol at 70–75° and the soluble material obtained by cooling the solution. The crystals thus obtained were again extracted in the same manner and the less soluble material (R salt) discarded. The crystals were dried in *vacuo* over sulfuric acid; titration with diazotized p-nitraniline showed them to be 94.7 to 95.3% pure. The absence of any large amounts of R and Schaeffer's salts was demonstrated by the fact that no color developed with diazotized sulfanilic acid in a buffer of P_H 5.6 and at a concentration of reactants at which both these salts couple rapidly.

Preparation of Solutions.—The results of the analyses given above were the basis for the preparation of the solutions of the sulfonated naphthols; it was assumed that the rest of the material was inert inorganic salt.

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[2] **Ann., 247,** 341 (1888); *Ber*., **24,** 3160 **(1891)**; *ibid*., 18, 46 (1885).

The diazonium salt solutions were always freshly prepared by diazotizing a solution of the corresponding amine at 0°. A solution of the amine of known concentrarion in standard hydrochloric acid was prepared and treated with sodium nitrite in the usual way. The concentration of the amine was usually 0.20 molar, the acid 0.52 molar. After the addition of the requisite amount of 0.20 M sodium nitrite (standardized by titration), the mixture was kept at 0° for about fifteen minutes and then diluted with water so that the resulting solution was 0.02 M in diazonium salt (it being assumed that the diazotization was quantitative) and about 0.012 M in free hydrochloric acid. This low concentration of hydrochloric acid may be still further decreased by the cautious addition of standard sodium hydroxide but this was not usually done since the high concentration of the buffering salt in the reaction mixture was sufficient to neutralize the small amount of free acid without materially affecting the PH of the mixture. In the diazotization of sulfanilic acid the material was dissolved in just as little ammonia as possible (60–70 cc. of 8 *M* NH_4OH per mole) and the solution diluted to a 0.50 molar solution. Ten cc. was then rapidly acidified with 10 cc. of 1.566 M hydrochloric acid at 0° and 10 cc. of 0.50 molar nitrite slowly added. After shaking for three hours at 0°, the mixture was diluted to 100 cc. The resulting solution was 0.050 M in diazonium salt and approximately 0.006 M in free hydrochloric acid, if there were no excess of ammonia in the initial solution.

Colorimeter.—A Campbell–Hurley colorimeter[3] was modified so that one of the two tubes was placed in a small thermostat the temperature of which was kept constant within 0.03". The tube fitted through a hole in the bottom of the thermostat box and was made water-tight by means of a rubber gasket. The other tube which was connected with the glass piston contained the standard solution and was not thermostated. Light from a 75-watt "daylight lamp" passed through a ground glass plate onto the mirror which reflected the beam through the two tubes. By moving the piston up and down the level of the standard solution was altered; the comparison of the two colors was made by means of the mirror and telescope characteristic of this type of colorimeter. Exactly 50 cc. of reaction mixture was always placed in the thermostated tube and the color matched by changing the level of the standard solution in the other tube, which was graduated from 1 to 100 cc. The readings of the level of the solution in this tube were a measure of the extent of the reaction.

Procedure

A color standard was first prepared from a reaction mixture (identical with the one under investigation) which had been allowed to stand at room temperature for at least fifteen hours to insure complete reaction. (Calculations using the velocity constants found and the temperature coefficient showed that the reaction would be 99% complete in less than twelve hours in every case.) Such a solution was diluted with an equal volume of the buffer solution and placed in the tube connected with the movable piston. The readings of the level in this tube (1 to 100) then corresponded directly to the extent of the reaction in the other tube. The validity of such a standard was shown by preparing many and comparing them with each other from time to time and also by allowing some reactions to proceed practically to completion, when the reading was found to be 100% within the experimental error. Although one standard might

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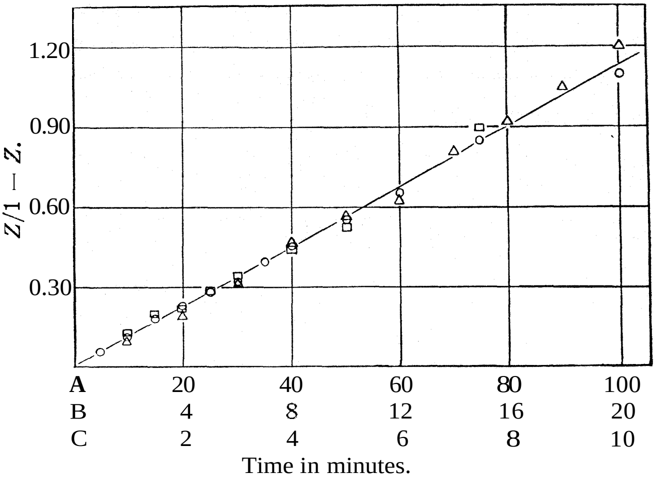
[3] Campbell and Hurley, THIS JOURNAL, 33,1112 (1911).

be used for many experiments days apart, fresh standards were actually prepared for each set of measurements. It is not possible to use a standard in one buffer for comparison with a reaction mixture in another buffer, as there is often a perceptible change in shade.

After the color standard had been introduced into one tube 48 cc. of buffer solution and 1 cc. of a solution of the hydroxy compound of requisite strength were placed in the other tube in the thermostat. After thermal equilibrium was established (twenty to thirty minutes), 1 cc. of the dilute diazonium salt solution, which had been kept in the thermostat for a short time, was rapidly introduced by means of a rapid-delivery pipet which reached to the bottom of the tube and through which a gentle stream of air was blown for a few seconds to stir the mixture. The time of mixing is estimated as less than five seconds. The time was recorded with a stop watch. Readings were usually made every minute for the first eight and then every two or three minutes, except in the case of very slow reactions. As a rule the measurements were continued until the reaction was 70–75% complete. The corresponding readings in duplicate experiments agreed well within **2** units (an error of 10 for 20% reacted).



□, Scale **A**, 0.0001 M; ○, Scale B, 0.0005 M; A, Scale C, 0.001 M.

Fig. 1.—Graphical representation of the rate of reaction of diazotized sulfanilic acid with sodium 1-naphthol-4-sulfonate. Equimolecular concentration of reactants. *P*H, 4.50; μ, 0.24; temp., 15°; slope, 0.0112; k, 112.

Results

Over a wide range of concentrations the reaction rate corresponds closely to the usual bimolecular equation. When the two reactants are present in equal amounts this takes the form of Equation 1 where C is the concentration of the reactants and Z the fraction reacted in the time, t (in minutes).

$$kC = \frac{1}{t}\frac{Z}{1 - Z} \tag{1}$$

The results of a number of experiments with diazotized sulfanilic acid and sodium 1-naphthol-4-sulfonate at PH 4.5 are shown graphically in Fig. 1. The value of $Z/(1 - Z)$ is plotted against t. The points fall well on a straight line which corresponds to a value of 112 for k. The same components taken in different proportions under the same conditions give results shown in Fig. 2. The integrated equation here takes the form of Equation 2, where C is the concentration of the reactant present in smallest amount, m the ratio of the two reactants (a whole number) and Z the fraction which has reacted.

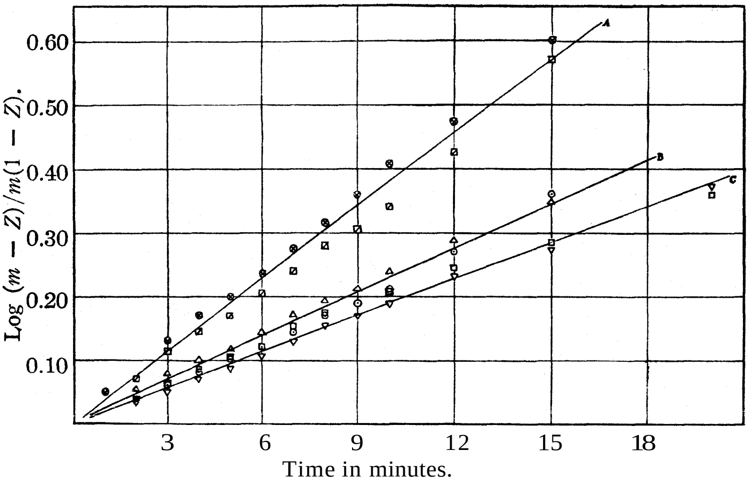


Fig. 2.—Graphical representation of rates of reaction of diazotized sulfanilic acid with sodium I-naphthol-4-sulfonate at **varying** concentrations of reactants. *PH*, 4.50; temperature, 15°; μ, 0.24.

	A		B		C	
Concn. (diaz.)	0.0001	0.001	0.0005	0.001	0.0001	0.0005
Concn. (naphthol)	0.001	0.0001	0.001	0.0005	0.0005	0.0001

$$\frac{C\,(m - 1)}{2.30}\,k = \frac{1}{t}\log\frac{m - Z}{m\,(1 - Z)} \tag{2}$$

In Fig. 2 the value of $\log (m - Z)/[m(1 - Z)]$ is plotted against t. The slopes of the three lines (A, B, C) correspond to values of k of 105, 111 and 112, respectively, all in excellent agreement with each other and with the value obtained in the experiments in which equimolecular proportions of the reactants were employed. Similar results were obtained with other pairs of reactants in different buffer solutions; some of these are collected in Table II. The values of k were determined graphically as illustrated

TABLE II

REACTION VELOCITY CONSTANTS OBTAINED IN EXPERIMENTS WITH VARYING CONCENTRATIONS OF REACTANTS

Temp., 15.0° Ionic Strength, 0.24

Reactants	P_H	Concn. in moles per liter × 10^3 Diazo salt	Hydroxy compound	k
Diazotized o-anisidine + disodium-2-naphthol-3,R-disulfonate	8.17	0.1	0.5	1000
	8.17	.1	.1	950
	8.17	.1	.1	970
Diazotized sulfanilic acid + disodium-2-naphthol-3,6-disulfonate	5.27	.5	1.0	95.6
	5.27	.1	0.5	97.5
	5.80	.1	.1	317
	5.80	.1	.5	350
	5.80	.5	.1	302
Diazotized sulfanilic acid + sodium *p*-phenolsulfonate	8.17	.1	.5	6.55
	8.17	.5	1.0	7.13
	8.17	.5	0.5	6.93
Diazotized aniline + disodium-1-naphthol-3,8-disulfonate	7.08	.5	.1	47.4
	7.08	.5	.5	52.7
	7.08	.1	.1	54.6

by Figs. 1 and 2. From all these results it is quite clear that the reaction is unusually free from complications and the rate is very closely expressed by the bimolecular equation.

The relationship between the rate of the reaction and the hydrogen-ion activity of the medium is shown in the results given in Table III and Fig. 3. Usually at least three experiments were performed with varying proportions of reactants, one in which equimolecular amounts were present and two in which the hydroxy compound was present in a 2 to 1 and 5 to I excess, the concentration of diazonium salt being 0.0005 and 0.0001 M, respectively. The value of k in each experiment was determined graphically. The range of the values of k thus obtained is given in the fourth column of Table III. It is evident from Fig. 3 that the values of log k fall closely on a straight line with unit slope. The reaction may thus be expressed by Equation 3

$$\log k = \log k_0 + P_H \tag{3}$$

In the sixth column of Table III are given the values of k calculated from the best fit of Equation 3 to the data; the assumed value of k_0 is given in each case in the cross heading. The difference between the calculated and observed values is given in the last column. The agreement is within the experimental error (± 7%). It should be noted that in the case of the two acetate buffers of P_H 4.5 (see Table I) the concentration of base (acetate ion) and of free acid have been varied five-fold without changing the rate. This is of importance as showing that the hydrogen-ion activity (or something directly proportional to it) is the controlling factor.

TABLE III

RATE OF COUPLING IN DIFFERENT BUFFER SOLUTIONS

Temp., 15°; ionic strength, 0.24

PH	Buffer (see Table I)	No. of Expts.	Range of values of k	Av. k	k (calcd. from Eq. 3)	Deviation, %
(1) Diazotized o-Anisidine + 2-Naphthol-3,6-disulfonate; $k_0 = 6.28 \times 10^{-6}$						
6.30	Phosphate II	2[a]	11.7–12.8	12.3	12.4	+1
7.08	Phosphate IV	2[b]	68–73	70.5	75.5	+0.7
8.17	Borate I	3	950–1000	975	930	−5
(2) Diazotized o-Anisidine + 1-Naphthol-4-sulfonate; $k_0 = 1.43 \times 10^{-5}$						
5.80	Phosphate I	3	7.9–9.1	8.32	9.0	+8
6.30	Phosphate II	3	28.8–32.4	30.5	28.5	−7
6.73	Phosphate III	4	64.9–74.0	71.5	76.0	+6
7.08	Phosphate IV	3	152–165	158	170	+8
(3) Diazotized Sulfanilic Acid + 2-Naphthol-3,6-disulfonate; $k_0 = 5.06 \times 10^{-4}$						
4.94	Phthalate II	3	33–39.8	37.4	43.5	+14
5.27	Acetate III	2[c]	95.6–97.5	96.5	95.0	−1
5.80	Phosphate I	4	302–350	330	318	−4
(4) Diazotized Sulfanilic Acid + 1-Naphthol-4-sulfonate; $k_0 = 3.55 \times 10^{-3}$						
4.50	Acetate I	6	104–113	111	112	+1
4.50	Acetate II	2"	106–109	108	112	+4
4.94	Phthalate II	3	287–317	304	308	+1
5.27	Acetate III	4	648–690	665	660	−1

[a] Duplicate experiments only (no variation in concentration of reactants). [b] One expt. 0.0005 M (naphthol), 0.0001 M (diazo.); other, 0.0005 M each. [c] One expt. 0.0005 M (naphthol), 0.0001 M (diazo.); other expt. 0.001 M in naphthol and 0.0005 M diazo.

In addition to determining the effect of changing hydrogen-ion activity on the rate, two other variables were studied. In a number of cases the reactions were carried out at both 15 and 25° and in this way a temperature coefficient of the reaction velocity obtained. The results are summarized in Table IV. It is clear that there is nothing unusual about the temperature coefficient of this reaction. The consistency of the results is indicated in Part 2 of Table IV by the fact that the values of E determined at three different PH values agree within the experimental error, which we estimate to be ±500 cal. Probably the variations in E with the different pairs of components is to be attributed to experimental error except in the first case reported, where the value seems to be larger than the average. In all the experiments which we have been considering the ionic strength of the solutions was kept constant at 0.24. A few experiments were carried out to obtain a preliminary idea concerning the nature of the salt effect. A series of acetate and phosphate buffers of constant PH and varying ionic strength were prepared. The ionic strength of these buffers was varied from 0.022 to somewhat more than 1.0. In all the cases studied (4 combinations) an increase of the ionic strength from 0.25 to 0.9 had little effect on the reaction rate. Thus for practical purposes one may probably ignore the salt effect within an accuracy of ±10% in the value of k. We had hoped by decreasing the ionic strength of the solution to obtain data which could be interpreted by means of Brönsted's theory.[4] However, because of the necessity of having the solutions sufficiently buffered it was impossible to work with solutions more dilute than an ionic strength of about 0.022. This is hardly dilute enough for us to obtain the real limiting slope to a curve representing the change of log k with change in the square root of the ionic strength. The results obtained in the region between $\sqrt{\mu} = 0.15$ and 0.5 we have not been able to interpret according to Bronsted's theory by any mechanism we have been able to devise. This aspect of the research must be investigated further before any definite conclusions can be drawn. It is enough at this time to mention the fact that diazotized o-anisidine + 1-naphthol-4-sulfonate showed no salt effect whatsoever either in concentrated or dilute solution. The other three pairs, diazotized *o*-anisidine + 2-naphthol-3,6-sulfonate, diazotized sulfanilic acid + 2-naphthol-3,6-sulfonate, and diazotized sulfanilic acid + 1-naphthol-4-sulfonate, show a considerable salt effect in the dilute range, the value of log k increasing by about 0.18 from $\sqrt{\mu} = 0.15$ to 0.5.

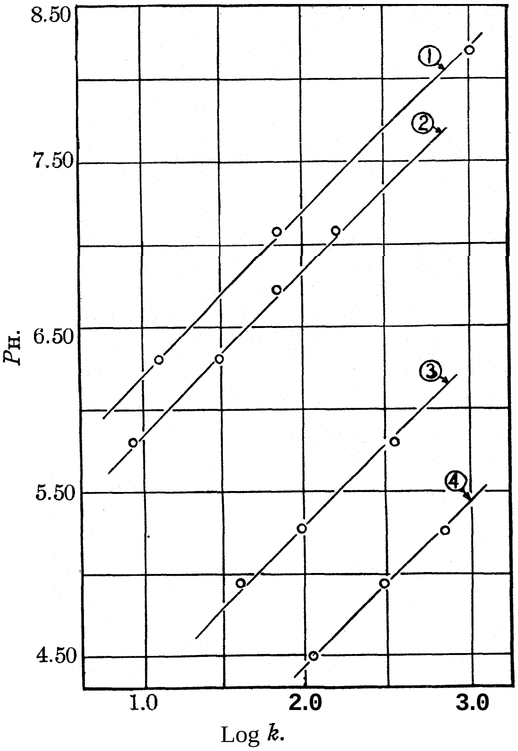


Fig. 3.—Rate of coupling of four pairs of components at different PH values. Temp., 15.0°; μ, 0.24. 1, Diazotized o-anisidine + R salt; 2, diazotized o-anisidine + N. and W. salt; 3, diazotized sulfanilic acid + R salt; 4, diazotized sulfanilic acid + N. and W. salt.

Relation between Chemical Constitution and Coupling Tendency

In order to save space we have summarized in Table V all the final values

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[4] J. N. Brönsted, *Chem. Rev.*, 5, 265 (1928); *Z. physik. Chem.*, 102, 169 (1923); *ibid.*, 115, 337 (1925).

TABLE IV

DETERMINATION OF TEMPERATURE COEFFICIENT OF CERTAIN COUPLING REACTIONS

PH	Concn. of naphthol, mole per liter	Concn. of diazo, mole per liter	$k_{15°}$	$k_{25°}$	$k_{25°}/k_{15°}$	E, cal.
(1) Diazotized o-Anisidine + R Salt						
7.08	0.0005	0.0005	78	208	2.66	16,700
7.08	.0005	.0001	71	195	2.75	17,200
(2) Diazotized o-Anisidine + N and W Salt						
5.80	.001	.0005	8.2	19.7	2.40	15,000
6.30	.0005	.0005	30.5	76.5	2.51	15,500
6.73	.0005	.0005	73	185	2.54	15,900
(3) Diazotized Sulfanilic Acid + R Salt						
5.27	.001	.0005	95.6	230	2.41	15,000
5.27	.0005	.0001	97.5	223	2.29	14,200
(4) Diazotized Sulfanilic Acid + N and W Salt						
4.50	.0005	.0005	108	262	2.42	15,100
4.50	.0005	.0001	116	272	2.34	14,600

In all the experiments acetate and phosphate buffers of the same ionic strength (0.24) were employed. The rates were measured at 15 and 25° in the same buffer solution on the same day. The value of E was calculated from the equation $2.303 (\log k_2 - \log k_1) = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$.

of k obtained in all the measurements carried out at ionic strength 0.24 and 15°. These include the combinations with 5 amines and 4 naphthols. The values of k given in the fifth column are averages of at least three different experiments in each of which the value of k was obtained graphically as illustrated in the cases given in full above. The measurements were always made between 8 and 70% reaction, an average of at least ten observations being made in each experiment. The average range of the values of k may be taken as ±7%, although in many cases the agreement was even better. In the two cases indicated by stars (*) measurements were made in quite alkaline solutions. The reaction in this case did not follow the bimolecular equation. There was a definite falling off in rate as the reaction proceeded. The numbers given are thus mere approximations to a mean rate. In all other cases the measurements agreed within the experimental error with the bimolecular formulation.

A convenient method of comparing the results obtained with a given pair of substances in two or more buffers is to calculate the PH at which k = 10 (log k = 1), assuming the linear relationship between log k and PH. This has been done in every case in Table V and the results are given in the last column. It is evident that in every case except the two in which the results are uncertain there is excellent agreement between the values obtained in the different buffers. Thus the relationship between rate of

TABLE V

SUMMARY OF DATA OBTAINED IN COUPLING EXPERIMENTS WITH A VARIETY OF NAPHTHOLS AND DIAZOTIZED AMINES (TEMP., 15.0°; IONIC STRENGTH, 0.24)

Amine	Phenol or naphthol	Buffer	P_H	Reaction velocity constant, k	Calcd. P_a at which k = 10
Sulfanilic acid	Sodium p-phenol sulfonate	Borate	8.17	6.85	8.34
		Borate	9.15*	31.6*	8.65*
Sulfanilic acid	Disodium 2-naphthol-6,s-disulfonate (G salt)	Phosphate	6.30	6.93	6 46
		Phosphate	7.08	35.5	6.53
Sulfanilic acid	Disodium 1-naphthol-3,8-disulfonate (Epsilon salt)	Phosphate	5.80	78.4	4.90
		Phthalate	4.94	9.5	4.96
Sulfanilic acid	Disodium 2-naphthol-3,6-disulfonate (R salt) .	Phosphate	5.80	330	4.28
		Acetate	5.27	96.5	4.29
		Phthalate	4.94	39.8	4.34
Sulfanilic acid	Sodium 1-naphthol-4-sulfonate (N and W salt)	Phthalate	4.94	305	3.46
		Acetate	5.27	660	3.45
		Acetate	4.50	110	3.46
Sulfanilic acid	Resorcinol	Acetate	4.50	118	3.43
		Acetate	5.27	810	3.36
p-Toluidine	Disodium 2-naphthol-6,8-disulfonate (G salt)	Borate	8.17	15.8	7.97
		Borate	9.15*	72.0*	8.29*
p-Toluidine	Disodium 1-naphthol-3,8-disulfonate (Epsilon salt)	Borate	8.17	200	6.87
		Phosphate	7.08	19.7	6.79
p-Toluidine	Disodium 2-naphthol-3,6-disulfonate (R salt)	Phosphate	6.73	165	5.51
		Phosphate	5.80	12.7	5.70
p-Toluidine	Sodium 1-naphthol-4-sulfonate (N and W salt)	Phosphate	6.30	95.0	5.32
		Phosphate	6.73	282	5.28
o-Anisidine	Disodium 1-naphthol-3,8-disulfonate (Epsilon salt)	Borate	8.17	62.5	7.36
		Phosphate	7.08	5.58	7.33
o-Anisidine	Disodium 2-naphthol-3,6-disulfonate (R salt)	Borate	8.17	985	6.18
		Phosphate	6.30	12.5	6.19
		Phosphate	7.08	71.1	6.23
o-Anisidine	Sodium 1-naphthol-4-sulfonate (N and W salt)	Phosphate	5.80	8.32	5.88
		Phosphate	6.30	31.0	5.81
		Phosphate	7.08	158	5.88
		Phosphate	6.73	71.2	5.88
Aniline	Disodium 1-naphthol-3,8-disulfonate (Epsilon salt)	Phosphate	7.08	50.2	6.38
		Phosphate	6.30	8.10	6.39
Aniline	Disodium 2-naphthol-3.6-disulfonate (R salt)	Phosphate	5.80	35.7	5.25
		Acetate	5.27	10.5	5.25
Aniline	Sodium 1-naphthol-4-sulfonate (N and W salt)	Phosphate	5.80	125.8	4.69
		Acetate	5.27	35.5	4.72
Aniline	Disodium 2-naphthol-6,8-sulfonate (G salt)	Borate	8.17	33.8	7.64
		Phosphate	7.08	3.19	7.58
p-Bromoaniline	Disodium 2-naphthol-6,s-disulfonate (G salt)	Phosphate	6.73	36.0	6.17
		Phosphate	5.80	5.63	6.06

TABLE V (Concluded)

Amine	Phenol or naphthol	Buffer	PH	Reaction velocity constant, k	Calcd. PH at which k = 10
p-Bromo-aniline	Disodium 1-naphthol-3,8-disulfonate (Epsilon salt)	Phosphate	5.80	107	4.77
		Acetate	5.27	31.7	4.77
p-Bromo-aniline	Disodium 2-naphthol-3,6-disulfonate (R salt)	Phosphate	5.80	222	4.45
		Acetate	5.27	62.2	4.48

All the experiments were carried out at 15° in buffered solutions of constant ionic strength (0.24) and measurements made between 8–10% reaction and 70–75% reaction. The values of k enumerated in the fifth column are averages of at least three experiments: one in which the components were in equivalent amounts, one in which the ratio of the reactants was in 2 to 1 (naphthol in excess) and one in which the reactants were 5 to 1 to each other (naphthol in excess). An average of 9 or 10 observations was made in each experiment. As indicated in Table II the average range in the value of k may be taken as ±7%.

coupling and hydrogen-ion activity illustrated in detail in Table III clearly holds in the case of all the substances investigated.

It is a matter of great interest to see to what extent it is possible to relate the coupling tendency of various compounds to their structure. As a measure of this coupling tendency one might use the value of log k_0 in Equation 3, but a somewhat more advantageous method of presenting the same results is to consider the PH at which log k has a definite value, for example 1. We may designate this PH as the "coupling value" of the pair of substances investigated at 15° and $\mu = 0.24$. It is evident that if one knows the coupling value for a pair of components it is possible to calculate the rate of reaction at any PH provided the ionic strength is fairly close to 0.24. Since the reaction follows the bimolecular equation so closely, the reaction velocity constant thus calculated may be turned directly into percentage reacted at a given time, provided the concentrations are specified. Furthermore, the rate at any temperature other than 15° may be estimated by using the usual equation for the temperature coefficient of the reaction velocity constant and a value of E of 15,000.

The coupling value of a given pair of components is determined both by the nature of the diazotized amine and the hydroxy compound. We have found that it is possible to assign constants to each amine and hydroxy component such that the sum of these numbers is approximately equal to the coupling value when the amine is diazotized and allowed to react with the hydroxy compound in question. This is illustrated by Table VI, in which the coupling value for each pair of components is given as calculated from a simple additive relationship of the two constants *A* and B arbitrarily assigned to the diazotized component and the hydroxy component, respectively. It will be noted that the agreement between the calculated and found coupling values is within a few tenths of a *P*H unit except in a few cases; that is, one may predict the rate from constants assigned to the individual components within an accuracy of 25%.

TABLE VI

COMPARISON OF THE COUPLING VALUE CALCULATED FROM THE EMPIRICAL CONSTANTS AND FOUND EXPERIMENTALLY (TEMP., 15°, $\mu = 0.24$)

	Sulfanilic acid, $A = 0$		*p*-Bromo-aniline, $A = 0$		Aniline, $A = 1.1$		*p*-Toluidine, $A = 1.5$		*o*-Anisidine $A = 2.1$	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1-Naphthol-4-sulfonate, $B = 3.5$	3.5	3.45			4.6	4.70	5.0	5.31	5.6	5.85
2-Naphthol-3,6-disulfonate, $B = 4.2$	4.2	4.28	4.2	4.43	5.3	5.22	5.7	5.60	6.3	6.22
1-Naphthol-3,8-disulfonate, $B = 5.1$	5.1	4.90	5.1	4.77	6.2	6.37	6.7	6.83	7.3	7.35
2-Naphthol-6,8-disulfonate, $B = 6.4$	6.4	6.46	6.4	6.10	7.5	7.60	7.9	8.02		
p-Phenol-sulfonate, $B = 8.3$	8.3	8.35								

The numbers given above for each pair of components represent the coupling value (PH at which log k = 1) as calculated according to the relationship $A + B =$ coupling value, and found experimentally as shown in Table V. The values of A and B for each component are given under the name and were assigned empirically so that the best agreement would result in this table.

In addition to the values given in Table VI, mention should perhaps be made of some very preliminary experiments which resulted in the assignment of the following constants: *p*-nitro-aniline, $A = -2$; salicyclic acid, $B = 8$; resorcinol, $B = 3.4$. To determine the coupling value of a pair of components within half a PH unit it is not necessary in most cases actually to use a colorimeter. By working with carefully prepared solutions of known concentration and a series of graduated buffer solutions, it is possible in a series of test-tube determinations to give a very good estimate of the coupling value. If these values and the corresponding constants for the individual components have analytical or preparative application, the advantage of such a series of rough colorimetric measurements is obvious.

In interpreting the significance of the constants A and B of Table VI one needs to know the mechanism of the reaction. It seems probable that the reaction proceeds according to the following scheme although, as was stated above, an attempt to apply this mechanism to an explanation of the primary salt effect has not been successful.

$$\text{Ar N}_2\text{X} + \text{OH}^- \rightleftharpoons \text{Ar N=NOH} + \text{X}^- \quad \text{(Fast and reversible)}$$

$$\text{ArN=NOH} + \text{P} \longrightarrow \text{Ar N=NP} + \text{H}_2\text{O} \quad \text{(Relatively slow and irreversible)}$$

In the two equations Ar represents an aromatic residue and P a phenol or naphthol. The equilibrium in the first step would be a function of the hydroxyl-ion activity, which is a direct function of the measured PH of the solution. Since the rate of the second step depends on the concentration of ArN=NOH this rate would be a function of the PH value of the buffer. The empirical constant *A* would seem to be a measure of the position of the equilibrium in the first step, while the empirical constant B corresponds to the speed of the reaction of the hydroxy compound in the second step. The fact that these two constants are approximately additive in every case would seem to indicate, in terms of the mechanism given above, that the rate of reaction of a diazo hydroxide and a hydroxy compound was a function only of the nature of the hydroxy compound. An inspection of Table VI makes it evident that there is greater regularity in the effect of change of chemical structure on the constant *A* than on the constant B. This is in accord with the fact that the relationship between equilibrium constants and structure is usually more regular than the relationship between structure and reaction velocity constants.

Whether or not the mechanism given above is correct, it is evident that it is possible to reduce to a remarkably simple formulation the reaction between diazotized amines and hydroxy compounds in dilute solution.

Summary

1. The rate of coupling of diazotized amines with certain phenols and naphthols has been measured colorimetrically in buffer solutions of constant ionic strength. Over a wide range of concentration the reaction rate corresponds to that calculated by means of the usual bimolecular equations.

2. The rate of coupling is a simple function of the hydrogen-ion activity of the buffer solutions. Each pair of components may be characterized (at a given temperature and salt concentration) by means of a "coupling value" defined as the P_H at which $\log k = 1$. In the case of the 20 pairs of components studied, it was found possible to assign certain empirical constants to each amine and phenol such that the sum was approximately equal to the coupling value.

3. The temperature coefficient was measured between 15 and 25°; the average value of E was 15,000. Some preliminary experiments indicate that the salt effect between the ranges $\sqrt{\mu} = 0.5$ and 0.9 may be neglected for practical purposes but from $\sqrt{\mu} = 0.5$ to 0.2 there may be considerable decrease in the velocity constant. Attempts to interpret the data in terms of Bronsted's theory have not yet been successful.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

STUDIES IN THE CHLOROPHYLL SERIES. II. REDUCTION AND CATALYTIC HYDROGENATION

BY J. B. CONANT AND J. F. HYDE

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The relationship between the magnesium-free chlorophyll derivatives and the porphyrins is a matter of considerable interest. While the structure of the porphyrins has been established by H. Fischer,[1] the constitution of the first decomposition products of chlorophyll (*e. g.*, the phaeophorbides, chlorin *e* and rhodin g) is still unknown. At the time this work was undertaken the only method of transforming the chlorophyll compounds into porphyrins was by means of drastic alkaline decomposition as employed by Willstatter. Within the last year several new reactions have been discovered which lead to the production of porphyrins from the chlorophyll series. The formation of a porphyrin in the pyrolysis of chlorin *e* was discussed in the first paper of this series.[2] In the course of the quantitative studies reported in the present paper, we have found that the complete hydrogenation of the chlorophyll compounds yields leuco compounds which on reoxidation with air form a mixture containing porphyrins. Fischer and Baumler[3] previously had discovered that a porphyrin is obtained by reducing phaeophorbide *a* with hydrogen iodide or sodium amalgam and reoxidizing with air. These transformations show the close relationship between the chlorophyll compounds and the porphyrins and seem to exclude the possibility suggested by Willstätter that the change from the one series to the other involved the synthesis of the carbon skeleton of the fourth pyrrole nucleus.

The characteristic structure of the porphyrins as given by Fischer contains a closed completely conjugated system of double linkages which includes linkages within and without the modified pyrrole nuclei.[4] Probably

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[1] See particularly H. Fischer and A. Treibs, **Ann., 466, 188** (1928), and **H.** Fischer and Schormiiller, *ibid.*, **473, 212 (1929).**

[2] Conant and Hyde, *Science*, 70,1806 **(1929);** THIS JOURNAL, **51,3668 (1929).**

[3] Fischer and Baumler, *Sitzb.* d. *Bayr.*, *Akademie d. Wissenschaften*, March, **1929,** p. 77; this paper had not come to our attention when our note in *Science* (Ref. **2)** was published; see also ***Ann.***, 474, 65 **(1929).**

[4] Professor Linus Pauling has suggested to us that the characteristic spectrum of a porphyrin, which consists of a number of relatively very narrow bands, is due to the cyclic system which encloses and protects the chromophoric groups from thermal disturbances; the porphyrins might thus be considered analogous to the rare earths. At his further suggestion we have examined the spectra of a number of porphyrins and chlorophyll derivatives at liquid-air temperatures and observed a narrowing of bands and in the case of the two porphyrins examined a resolution of bands into lines. The further study of this phenomenon which is now in progress may possibly be of some service in establishing the structural relationships between the chlorophyll series and the porphyrins.

because of the closed cyclic conjugated system the porphyrins are not as reactive as the majority of highly colored organic compounds. For example, the combination of gaseous hydrogen and colloidal palladium on asbestos suspended in aqueous alkaline solution will reduce to the corresponding leuco compounds all the common dyestuffs which we have examined. Sodium hydrosulfite will usually bring about the same change. The porphyrins, however, occupy an almost unique place among colored organic substances by virtue of the fact that they are not reduced in alkaline aqueous solution by either hydrosulfite or hydrogen with palladized asbestos. On the other hand, the chlorophyll derivatives (the phaeophorbides, chlorin *e*, rhodin g) are reduced, as is also the bile pigment bilirubin.

Experiments with Hydrosulfite.—In all the experiments with sodium hydrosulfite, 0.1 N potassium hydroxide was used and the concentration of the organic material was approximately 0.5×10^{-3} mole per liter. This concentration gave in most cases quite a highly colored solution. The solution of sodium hydrosulfite was approximately 0.01 molar in 0.1 N potassium hydroxide and was freshly prepared before each series of experiments were made, being kept under a layer of xylene. Even under these conditions the reducing power was lost very rapidly. The concentration was determined approximately before use by titrating with ammoniacal copper sulfate solution. The first experiments were carried out by placing two cc. (containing 0.001 millimole) of the alkaline solution of the organic material in one arm of an H-tube and placing the desired amount of hydrosulfite solution in the other. The tube was then repeatedly evacuated (five or six times), and filled with oxygen-free nitrogen. This precaution was taken since it was expected that any reduction product would be sensitive to air. The contents of the two sides were mixed by tilting the tube and the tube was examined at noted intervals to observe the color. It was soon found that no apparent change takes place at room temperature but that the color change is rapid when the tube is heated in the steam-bath. The later experiments were carried out in a silica test-tube, which avoided possible complications due to contamination by metals from the glass. In a blank test in which the same quantity of hydrosulfite was heated alone under otherwise identical conditions, it was found that the reducing power of the hydrosulfite was completely lost in twenty to thirty minutes, as shown by titration with ammoniacal copper sulfate solution.

Phaeophorbide *a* and chlorin *e* were reduced by sodium hydrosulfite at SO° in about ten minutes, yielding a pink solution which with air became green, while longer heating with excess hydrosulfite produced a similar green color. The green solutions were spectroscopically similar to but not identical with the initial solutions. Phaeophorbide b and rhodin *g* did not give a pink phase; there appeared to be a slight color change, but there was no clear indication of a further change on exposure to air. Isochlorophyllin (*a* plus b) showed no change. It is interesting that the introduction of magnesium prevents the action of hydrosulfite. Bilirubin changed from a light yellow-orange to a reddish-orange, which with air reverted to the yellow-orange. A rather broad absorption band in the green appeared on reduction; this disappeared on exposure to air, the spectrutn again being like that of the initial material.

Some idea of the minimum number of moles of hydrosulfite required to produce the changes was obtained from a series of experiments using varying proportions of hydrosulfite. Por example, with phaeophorbide a five moles per mole produced a definite brown color, whereas with three moles no noticeable change of the initial olive-green could be observed. The change with five moles was not so definite as with ten moles, and it would, thrrefore, appear that somewhere between these limits lies the minimum amount of hydrosulfite necessary to reduce this substance under these conditions. Approximately seven moles per mole of substance seemed to be required with the phaeophorbides, chlorin *e*, rhodin g and bilirubin. We cannot conclude from this, however, that these numbers correspond to a stoichiomctric relationship in the reduction process; a large excess of hydrosulfite may be required in order to obtain a sufficiently high rate of reaction or in order to compensate for the partial destruction of the hydrosulfite which occurs at this temperature.

It was evident from our experiments that both the typical porphyrins from the blood pigments (protoporphyrin and mesoporphyrin) as well as two porphyrins from chlorophyll (cyanoporphyrin and erythroporphyrin) were not affected by hydrosulfite at SO°, whereas the magnesium-free chlorophyll derivatives were attacked although they were not reduced to colorless compounds.

Reduction with Hydrogen.—The action of hydrogen in the presence of palladium on asbestos was studied in a special apparatus which enabled us to measure with a fair degree of accuracy the number of moles of hydrogen consumed even with such small samples as 3–6 mg. This apparatus, which was developed in this Laboratory, will be the subject of a separate paper, since it promises to be of value in connection with any problem involving absorption of hydrogen or oxygen by very small quantities of material. It was composed entirely of glass and the pressure differences were read on a differential scale as in the Warburg apparatus for measuring oxygen consumption.[5] The palladium catalyst was prepared by adding 10 cc. of a 1% solution of palladous chloride to a small amount of asbestos suspended in water and reducing with the required amount of hydrazine hydrochloride and alkali. The catalyst was filtered off, thoroughly washed and finally suspended in a total volume of 100 cc. of water. At the beginning of an experiment, 1-cc. portions of the suspension were added to the alkali contained in each of the two reaction bottles of the apparatus (one of which served as the blank control) which were connected by the differential manometer. The sample was contained in a small glass tube so arranged

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[5] Warburg, *Biochem. Z.*, 152, **51–63 (1924).**

that it could be broken *after* the equilibration of catalyst and solvent with hydrogen was complete. The apparatus was standardized by reducing well-known substances of high purity in aqueous alkali with hydrogen and palladium on asbestos. In a typical run 0.0148 millimole of quinone gave a final reading on the differential manometer of 4.6 cm. (the liquid in the manometer was oil of cloves), corresponding to 0.0026 millimole of hydrogen (at 23°, 760 mm.) per cm. The other results with the same compound gave 0.0025 and 0.0024. Indigo tetrasulfonate and anthraquinone disulfonate gave similar results. Dimethylacrylic acid in glacial acetic acid with a platinum oxide catalyst gave values of 0.0026 and 0.0027 millimole per cm.

The results obtained with the chlorophyll compounds and the porphyrins are summarized in Table I. As in the case of the experiments with sodium hydrosulfite it is clear that the porphyrins are different in their behavior from the magnesium-free chlorophyll derivatives and bilirubin. The small amounts of hydrogen recorded in the last column of Table I in the case of a few porphyrins are within the experimental error. Although the quantitative results were not entirely reproducible, it appears that the

TABLE I

SUMMARY OF RESULTS OBTAINED IN EXPERIMENTS ON THE ACTION OF HYDROGEN AND PALLADIUM CATALYST IN ALKALINE SOLUTION AT 23°

Substance	Millimole of substance	Millimole of H_2 absorbed	Approx. time in hours for reduction	Mole of H_2 per mole of substance
Phaeophorbide a	0.0068	0.0109	60	1.6
Phaeophorbide a	.0036	.0061	40	1.7
Phaeophorbide b	.0036	.0057	42	1.7
Phaeophorbide b	.0033	.0057	40	1.73
Chlorin e	.0052	.0096	36	1.8
Chlorin e	.0041	.0023	30	0.57
Chlorin e	.0028	.0018	42	0.6
Chlorin e	.0030	.0039	24	1.3
Chlorin e	.0078	.0100	49	1.3
Rhodin g	.0059	.0086	48	1.45
Rhodin g	.0018	.0028	50	1.6
Bilirubin	.0068	.016	35	2.3
Bilirubin	.0044	.0073	30	1.6
Cyanoporphyrin	.0089	.0032	15	0.36
Cyanoporphyrin	.0054	.00053	50	.10
Erythroporphyrin	.012	.00159	12	.13
Erythroporphyrin	.0065	.00035	48	.05
Protoporphyrin	.0054	.00	60	.00
Protoporphyrin	.014	.00	20	.00
Mesoporphyrin	.0057	.00	72	.00
Phylloporphyrin	.006	.00	20	.00

NOTE.—In calculating the millimoles of substance the following molecular weights were employed: phaeophorbide a, 610; phaeophorbide b, 624; chlorin e, 628; rhodin g, 611; bilirubin, 584.

phaeophorbides, chlorin e and rhodin g take up approximately two moles of hydrogen; the results with chlorin *e* were the least satisfactory. The reduction of the magnesium-free chlorophyll derivatives under these conditions does not lead to the formation of leuco compounds; the reduced solutions are still colored as in the case of the action of hydrosulfite. In this connection it should be pointed out that the reductions brought about by hydrogen in the presence of palladized asbestos are not catalytic hydrogenations but reduction processes at a level of intensity of the hydrogen electrode. Only special linkages are attacked by *reducing* agents as contrasted with *hydrogenating agents;* for example, neither sodium hydrosulfite[6] nor palladium on asbestos in alkaline solution with hydrogen will add hydrogen to such double bonds as those which occur in allyl alcohol and dimethylacrylic acid.

Catalytic Hydrogenation.—Although the porphyrins are not attacked by the two reducing agents just mentioned, they may be converted into leuco compounds by a number of procedures, as is well known. Fischer, for example,[7] catalytically reduced the methyl ester of uroporphyrin in acetic acid using a platinum catalyst. Kuhn[8] has also studied the catalytic reduction of the porphyrins in acetic acid solution and has shown that the leuco compounds formed are reoxidized to the same porphyrin on exposure to air. Using our same apparatus we have carried out a few experiments on the catalytic hydrogenation of the magnesium-free chlorophyll derivatives in acetic acid using the platinum oxide catalyst of Adams?

The results are summarized in Table II. In every case the final solutions were colorless and on exposure to air became colored again. A distinction of considerable importance between the phaeophorbides, chlorin e and rhodin g on the one hand, and the porphyrins on the other hand, is the fact

TABLE II

EXPERIMENTS ON THE CATALYTIC HYDROGENATION IN GLACIAL ACETIC ACID OF CERTAIN CHLOROPHYLL DERIVATIVES AND PORPHYRINS

Substance	Millimole of substance	Millimole of H_2 absorbed	Time of reduction in hours	Moles of H_2 per mole of substance
Phaeophorbide a	0.0058	0.0214	3	3.7
Phaeophorbide *b*	.0057	.0223	6	3.9
Chlorin e	.0068	.02407	12	3.54
Chlorin e	.00479	.01832	19	3.82
Rhodin *g*	.0052	.0182	18	3.5
Cyanoporphyrin	.0061	.01805	6	2.96
Erythroporphyrin	.0067	.0247	4	3.7
Phylloporphyrin	.0083	.0292	3	3.5

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[6] Conant and Cutter, J. Phys. *Chem.*, 28, 1096 (1924).

[7] Fischer and Zerweck, Z. *physiol. Chem.*, 137, 242 (1924).

[8] Kuhn and Seyffert, Ber., 61, 2509 (1928).

[illegible]dams and Shriner, THIS JOURNAL, 45, 2171 (1923).

that the chlorophyll derivatives did not revert to the original substances on shaking the reduced solutions with air, whereas the porphyrins were regenerated.

The oxidation product of the hydrogenated chlorophyll compounds is a complex mixture. Porphyrins appear to be formed as judged by the spectra of the products obtained after fractionating with hydrochloric acid according to the Willstatter–Mieg procedure.[10] We have isolated small quantities of two crystalline porphyrins from the hydrogenation of chlorin e in acetic acid and subsequent oxidation with air. The analyses and spectra are given below.

Porphyrin from chlorin e: acid number, about 0.7. Spectrum in ether (0.1 g. in 5 liters), 100-mm. layer: (very faint) 638—630; 593- - -587.6—575.8; 557.2- - -550—540.5- - -534.4; 523.8- - -520—492.4- - -488.4; E. A., 445.4.

Anal. Calcd. for $C_{34}H_{38}O_5N_4$: C, 70.0; H, 6.5. Found: C, 70.4; H, 6.6.

Porphyrin from chlorin e: acid number about 5. (Insufficient amounts for analysis.) Spectrum in ether, 100-mm. layer: (faint) 646.9—644; 635.4—630.3; 591.8- - -579.9—575.3; 561.3- - -559.0—548.5- - -544.9; 525.5- - -522.8—507.2; E. A. 444.1.

The resistance of the porphyrins to mild reducing agents as well as the fact that the leuco compounds are reoxidized and reconverted to the original material indicates a particularly stable arrangement of linkages in the porphyrin molecule. The behavior of the phaeophorbides, chlorin e and rhodin g shows clearly that they contain a more reactive unsaturated system. They appear to contain groupings which, like those present in the dipyrrylmethenes, are easily attacked by mild reducing agents. If one accepts the conclusion that the carbon skeleton of the porphyrins is already present in the phaeophorbides, it seems probable that one of the four modified pyrrole nuclei does not have its unsaturation so located as to form part of the cyclic conjugated system characteristic of porphyrins. As a result, the incompletely conjugated systems are readily attacked by mild reducing agents but on reoxidation of these products porphyrins are not formed. A drastic hydrogenation followed by oxidation is necessary before the porphyrin structure is formed. The quantitative results (Table II) show that the degree of total unsaturation of the porphyrins and chlorophyll compounds is the same as measured by the formation of the leuco compounds in acetic acid. The difference thus appears to rest in the location of the various linkages. Two relatively reactive double bonds are present in the chlorophyll series and one or two more that are only attacked by catalytic hydrogenation. These latter are part of the chromophoric group present in the colored *reduction* products of the chlorophyll series formed by the action of the mild reducing agents.

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[10] Willstätter and Mieg *Ann*, **350**, 1 (1906).

In connection with the experiments with hydrosulfite, we have made another observation which shows the reactivity of the chlorophyll compounds as compared with the porphyrins. When the phaeophorbides or chlorin e or rhodin *g* in ether solution are shaken with an aqueous solution of sodium acid sulfite, a rapid reaction takes place in which the intensity of the color is much diminished and the shade changes to a reddish-brown, some of the material passing into the aqueous layer. The porphyrins do not show this behavior. We propose to investigate this reaction further.

Summary

1. The action of sodium hydrosulfite in alkaline aqueous solution at 80° on chlorophyll derivatives and porphyrins has been examined. The magnesium-free chlorophyll derivatives are reduced with a change of color; the porphyrins and the magnesium-containing chlorophyll compound isochlorophyllin are not affected. Similar results were obtained with hydrogen and palladium on asbestos suspended in an aqueous alkaline solution at 23°. The amount of hydrogen absorbed was measured in a special micro apparatus. The magnesium-free chlorophyll compounds took up approximately two moles.

2. Catalytic hydrogenation of the porphyrins and the chlorophyll compounds proceeds to leuco compounds in glacial acetic acid. The number of moles of hydrogen absorbed is 3 to 4. On reoxidation with air the porphyrins are regenerated; the chlorophyll compounds yield a mixture of products including some porphyrins.

CAMBRIDGE, MASSACHUSETTS

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

AN INVESTIGATION OF THE BASES IN THE KEROSENE DISTILLATE OF CALIFORNIA PETROLEUM[1]

BY E. J. POTH,[2] W. A. SCHULZE,[2] W. A. KING,[3] W. C. THOMPSON,[3] W. M. SLAGLE,[4] W. W. FLOYD[4] AND J. R. BAILEY[5]

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Introduction

Very little is known regarding the nature of the nitrogen compounds in crude petroleum, and these are at times confused with products in *dis-*

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[1] This paper contains results obtained at the Chemical Laboratory, University of Texas, in an investigation on "The Nitrogen Compounds in Petroleum," listed as Project 20 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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[5] Director. American Petroleum Institute Project 20.

tillates that result from decomposition of more complex substances at distillation temperatures.[6] Whereas certain California crude petroleum, that uniformly has a high nitrogen content, yields practically no bases on acid extraction, crude distillates from this source contain bases readily extracted with mineral acids. However, along with bases there are present nitrogen compounds *inert to dilute mineral acids,* for the isolation of which methods have not been developed. In the kerosene distillate produced by the Union Oil Company of California from McKittrick asphalt crude petroleum, with a total nitrogen content of 0.055%, it was found that approximately 55% of the nitrogen compounds could be extracted with dilute sulfuric acid, and in the higher-boiling distillates, with the total nitrogen content greater, the proportion of basic to inert nitrogen compounds decreased with increase of the distillation temperature. The non-basic nitrogen compounds may be of the pyrrole type with the higher members indoles or carbazoles, or there is a further possibility of the occurrence here of heterocyclic compounds containing both nitrogen and sulfur.

The great complexity of the nitrogen compounds in petroleum and its crude distillates, the wide boiling point range of these distillates, all of which contain both basic and non-basic volatile nitrogen compounds, and finally the fact, developed in the present investigation, that exhaustive fractional distillation of California kerosene bases, which have a range of boiling points at atmospheric pressure from 180 to 335°, does not yield any of the components in pure form, make it quite probable that *petroleum offers the greatest wealth of nitrogen compounds of any natural source.*

That a number of substances constitute each of the numerous distillation fractions of kerosene bases is also revealed by the fact that so far in this investigation it has been found that, except as concerns distillation fractions in the 276° zone, picrates do not separate directly in crystalline form. Through the employment of (1) fractional extraction with a buffered acid solution and (2) fractional precipitation of the bases from the resulting acid solution with sodium hydroxide, it is possible, however, to concentrate individual components of the distillation fractions to the point where they form crystalline salts. In this way from 1560 cc. of distillation fractions, boiling at 249–252°, several products have been isolated in apparently pure form[7] and will be investigated later. However, the small, initial yields of these substances indicate quite conclusively that only repeated application of methods (1) and (2) will effect a separation of all the component bases.

It might be contended that failure of fractional distillation to yield

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[6] (a) Day, "Handbook of the Petroleum Industry," p. 529; (b) E. J. Poth, W. D. Armstrong, C. C. Cogburn and J. R. Bailey, Ind. Eng. Chem., 20, 83 (1928).

[7] This phase of the investigation has been developed by E. J. Poth and Ivy Parker.

individual products in pure form is due to the formation of *constant boiling mixtures* with the components differing within wide ranges of boiling points. The present investigation, so far as it has progressed, indicates, however, that fractional distillation yields mixtures of products, which even at atmospheric pressure boil within a range of a few degrees. Since the distillations, to prevent decomposition of the bases, are preferably carried out at low pressures, it is not at all improbable that with the reflux column it is possible to separate the bases in fractions with the components boiling at highly reduced pressure within a range of less than two degrees. In confirmation of this tentative claim it may be cited that in a fraction of bases under investigation there have been isolated in pure form two compounds of the formula, $C_{12}H_{13}N$, boiling at atmospheric pressure (746 mm.) at 280.6 and 278.9°, respectively, and a substance of the formula, $C_{16}H_{25}N$, boiling at 278.2°. What is equally conclusive of the claim advanced is that the residual bases in this fraction, after removal of the three products referred to, boil to the last drop at constant temperature, making impossible the use of fractional distillation in their separation. Furthermore, in the distillation of these residual bases, where several cuts are made, each shows the same refractive index. Undoubtedly several products here remain to be isolated in pure form, and it may be expected that all of them have boiling points in close proximity.

The only investigation of bases from California distillates thus far published was carried out by Mabery and Wesson,[8] and, regarding the source of their material, there occurs the following statement: "They were separated from California distillates by Peckham and Solathé by washing a large quantity of the *distillates* with dilute sulfuric acid and precipitating the bases with alkali."[9] Since no individual base was isolated by Mabery and Wesson, it is not surprising that some of their conclusions as to the structure of these products are disproved by the present investigation in the Texas Laboratory.

More recently from shale oil distillates there have been isolated and identified several alkylated pyridines.[10]

The first year on Project 20 was devoted to an exhaustive survey of the nitrogen content of petroleum from the most important oil fields of this continent and preliminary work in the location of the most available source of petroleum nitrogen compounds in quantity. The results of this phase of the work are embodied in part in a paper, entitled "The Estimation of Nitrogen in Petroleum and Bitumens."[11]

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[8] C. F. Mabery and L. G. Wesson, THIS JOURNAL, 42, 1014 (1920).

[9] C. F. Mabery, *J. Soc. Chem. Ind.*, 19, 505 (1900).

[10] Takashi Eguchi, Bull. *Chem. Soc. (Japan)*, 2, 176 (1927); 3, 227 (1928); C. A., 21, 3197 (1927); 23, 391 (1929).

[11] Ref. 6 a, p. 83.

In this investigation it developed, because of the amount of material to be handled, that only through the cooperation of some refinery, working petroleum of high nitrogen content, would it be practicable to assemble material sufficient in amount for an exhaustive investigation of petroleum nitrogen. Furthermore, it was equally evident that the desired cooperation would be extended only on condition that it would involve a minimum of inconvenience in plant operation.

In refining crude distillates either with sulfuric acid or liquid sulfur dioxide, practically all the contained nitrogen is eliminated from the finished products. However, in sulfuric acid refining, even if the nitrogen compounds are not sulfonated, polymerized or changed in other ways, the cost involved in their isolation from the acid extract would be very heavy. On the other hand, in the Edeleanu process the liquid sulfur dioxide apparently exerts merely solvent action, and, after recovery of the sulfur dioxide, the residue contains the nitrogen compounds admixed with a large quantity of hydrocarbon oil. From this residue the bases can be extracted with dilute sulfuric acid and the water-insoluble bases separated from the acid layer with caustic soda. It is probable that extraction with a suitable solvent would yield here at times water-soluble bases.

An arrangement was effected with the Union Oil Company of California whereby 150 barrels of the residue from refining their kerosene distillate with liquid sulfur dioxide were extracted with dilute sulfuric acid, and from this material 50 liters of water-insoluble bases, free of hydrocarbon oil and containing only a trace of sulfur, were obtained.[12]

The following information regarding the potential supply of petroleum nitrogen compounds was furnished by Mr. Haylett: Edeleanu residues represent about 30% by volume of the stock treated. Four companies in California equipped to use the process have a combined daily capacity of about 10,000 barrels of oil. While lubricating, transformer and spray oils are refined by this method, around 80% of the capacity is devoted to kerosene and similar distillates.

The Edeleanu residues do not represent waste products; they are valuable for the production of aromatic oils, employed as special solvents and, on account of their detonation suppressing qualities, are included, as far as boiling points permit, in motor fuels. One company uses Edeleanu residues in the manufacture of insecticides.

The present paper deals with a new base of the formula, $C_{12}H_{13}N$ (A),

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[12] Acknowledgment is due Mr. R. E. Haylett, Technical Assistant, Dr. Carl Iddings, Plant Chemist, and Mr. T. F. Ott, Lubricating Technologist of the Union Oil Companv, and also Research Fellow W. M. Slagle, for services rendered in preparing what is probably the largest amount of so-called petroleum bases ever assembled for investigation.

with its structure established as 2,3,8-trimethylquinoline. It occurs to the extent of about 18% in the fraction of kerosene bases boiling at atmospheric pressure around 276–277°. Only negligible amounts are present outside the range 274–280°. From the same fractions there have been isolated in pure form a second $C_{12}H_{13}N$ (B) base and a third base of the formula, $C_{16}H_{25}N$ (C). In addition, there occur in the same temperature zone several other bases for the isolation of which methods are now being successfully developed. Since only the investigation of 2,3,8-trimethylquinoline has been concluded, the other products will be reported on later.

With Base A assumed to be an alkylated quinoline, the structure was correctly deduced from its behavior toward (1) methyl iodide and (2) formaldehyde. Since it does not react at water-bath temperature with methyl iodide to form a quaternary ammonium salt, steric hindrance, due to substituents at positions 2 and 8, was inferred.[13]

With the known 2,4,8-trimethylquinoline[14] excluded, methyls at 2 and 3 were indicated by condensation of the base with ***two*** and not ***three*** moles of formaldehyde.[15]

Methyls in positions 2 and 3 were confirmed by the formation of a dimethylquinolinic acid in chromic acid oxidation of the $C_{12}H_{13}N$ base, in that this carboxylic acid on distillation with soda lime gave a product of the formula, $C_{11}H_{11}N$, identified as 2,3-dimethylquinoline.[16] Oxidation of the ***formaldehyde*** compound of the $C_{12}H_{13}N$ base also gave a dimethylquinolinic acid, converted by soda lime distillation to a new base, $C_{11}H_{11}N$, the structure of which as 3,8-dimethylquinoline was proved by its synthesis from o-toluidine, methylal and propionic aldehyde.[17]

Finally, through the Doebner–Miller synthesis,[18] 2,3,8-trimethylquinoline was prepared by the action of hydrochloric acid on a mixture of o-toluidine and tiglic aldehyde, and its identity with the kerosene base confirmed.

Since among the kerosene bases there are undoubtedly many components which are hydrides of alkylated quinolines or other heterocyclic complexes with the possibility of asymmetric carbon atoms present, it is of interest to note that an examination of all the different distillation fractions failed to reveal in any case optical activity. This applies also to the $C_{16}H_{25}N$ base, obtained in large amount from fractions in the 276° zone; this prod-

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[13] *Cf.* J. v. Braun, W. Gmelin and A. Petzold, *Ber.*, **57**, 389 (1924).

[14] S. Yamaguchi, *J. Pharm. Soc. (Japan)*, **503**, 23–33 (1924); *C. A.*, **18**, 1666 (1924).

[15] For literature references see Meyer and Jacobson's "Lehrbuch der Organischen Chemie," Vol. II, Part 3, p. 933.

[16] G. Rohde, *Ber.*, **20**, 1911 (1887).

[17] Acknowledgment is due G. R. Lake of the Texas Laboratory for this synthesis. *Cf.* Carl Beyer, *J. prakt. Chem.*, **33**, 419 (1886); W. v. Miller and Fr. Kinkelin, *Ber.*, **20**, 1916 (1887).

[18] *Cf.* O. Doebner and W. von Miller, *ibid.*, **16**, 2464 (1883).

uct is undoubtedly hydro-aromatic with the possibility of one or more asymmetric carbon atoms in the molecule.

Experimental Part

Fractional Distillation of the Kerosene Bases.—The apparatus employed in fractional distillation of the 50 liters of crude bases can be understood by reference to the accompanying figure.[19]

Through the use of mercury check-valves in the vacuum distillation receiver, stopcocks are entirely eliminated in the distillation train and contamination of the distillate with tap grease is obviated. The use of capillary leaks for pressure control proved more satisfactory than the expensive electrical devices usually employed in this connection.

In the largest type of apparatus used, B is a 5-liter flask sealed to C, a jacketed reflux column, which is packed with No. 18, double jack iron chain.[20] Provision is made for heating the reflux column by resistance wire circularly wound around the jacket, D. The support, E, at the

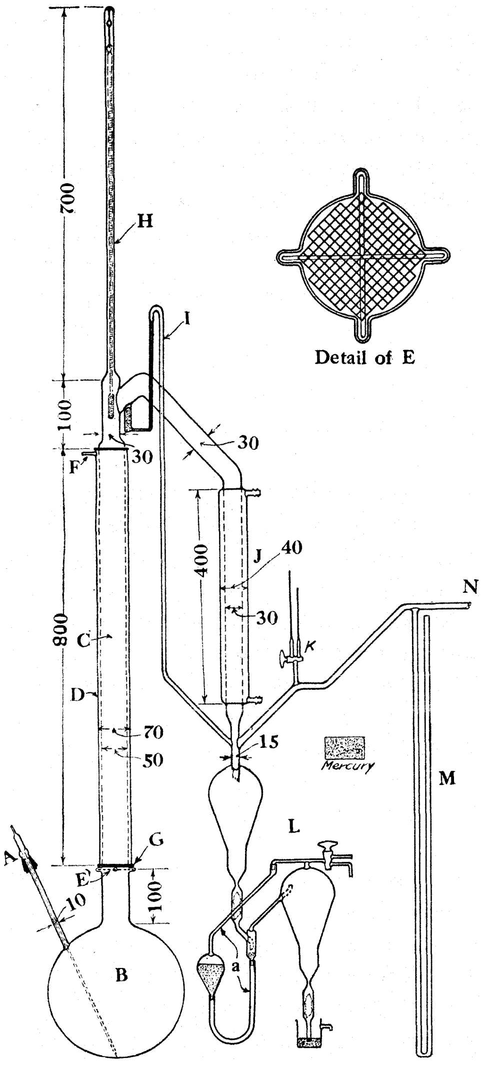

Fig. 1.—Vacuum distillation apparatus (pyrex glass, dimensions in millimeters). A, Ground-glass seal; B, 5-liter flask; C, still column (chain filling); D, column jacket; E, support for chain in column; F, air inlet to jacket; G, transite support for jacket; H, thermometer tube; I, capillary manometer; J, condenser; K, capillary leaks; L, receiver; M, manometer; N, lead to vacuum pump; 'a,' rubber tubing.

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[19] This apparatus was patterned after one in use at the Bureau of Standards by E. W. Washburn and J. H. Brunn in connection with Project No. 6. Acknowledgment is hereby given for a blue print of their apparatus. Acknowledgment is also due Research Fellow E. J. Poth for construction and operation of the stills in use as well as for innovations in the Washburn–Brunn apparatus, consisting of the manometer, I, capillary leaks, K, and receiver, L ["A Receiver for Vacuum Distillation," by Edgar Poth, *Ind. Eng. Chem. (Analytical* Ed.), 1, 111 (1929)], shown in accompanying figure.

[20] This chain is manufactured by the Corbin Screw Corporation, New Britain, Conn.

lower end of C contains four protrusions, into which lead heavy iron wires supporting a wire gauze on which rests the coiled chain. The ground-glass seal, **A**, serves for charging or cleaning B and is extended in the form of a bubble tube of the ordinary type used in vacuum distillation to obviate bumping. Three-way stopcock K affords an air intake through capillaries which were regulated so as to provide in the system pressures of either 4 or 11 mm. The lower pressure was used with high-boiling residues to obviate as far as possible decomposition of the bases.

The rate of distillation was kept as near one drop a second as possible, this being regulated, where necessary, either by forcing cold air into F or heating D through the resistance coil. All the material at hand was carried through six fractionations and, in the temperature zones where the largest amount of material was available, eight fractionations were made. After it became evident that fractional distillation alone would not lead to a separation of any of the bases in pure form, this procedure was supplemented by isolation of the bases through appropriate salts.

Isolation and Synthesis of 2,3,8-Trimethylquinoline[21]

A very satisfactory method is to isolate this $C_{12}H_{13}N$ base in the form of the picrate, admixed with the picrate of base $C_{16}H_{25}N$, by the addition of successive portions of 20 g. of picric acid in 50 cc. of 50% acetic acid to 100 cc. of a distillation fraction in 350 cc. of 50% acetic acid. The picrate of the latter base, in contrast to that of the former, is readily soluble in both benzene and alcohol, and, therefore, a mixture of these salts is easily separated.

A second method of isolation of 2,3,8-trimethylquinoline is offered through its acid sulfate. Preliminary tests indicate the amount of 50% sulfuric acid to be used as well as the concentration of this base in different fractions. Through the sulfate test fractions boiling from 274 to 280° (748 mm.), inclusive, were found to contain 2,3,8-trimethyl quinoline with the maximum amount of around 20% in the 276–277° fraction. Since the sulfate of base $C_{16}H_{25}N$ is very soluble, it is not precipitated but can be subsequently separated as picrate. However, admixed with this sulfate there occurs in small amount the sulfate of a second $C_{12}H_{13}N$ base, as yet unidentified. This latter base is an odorless solid, melting at 43° and boiling at 278.9° (748 mm.). It reacts with formaldehyde and with methyl iodide forms the corresponding quaternary ammonium salt at water-bath temperature.

In an attempt to isolate the residual bases from the distillation fractions, in which the three components referred to above occur, experiments are under way in which fractional extraction with buffered solutions is employed. That this procedure will prove effective is indicated by the recovery of considerable amounts of the $C_{16}H_{25}N$ base that escaped isolation in the original picrate precipitation. The control conveniently employed in this process is the determination of refractive indices.

The following refractive indices, n_D^{60}, are of interest: (A) 2,3,8-trimethylquinoline, 1.5828; (B) $C_{12}H_{13}N$ base of unknown structure, 1.5828; (C) $C_{16}H_{25}N$ base, 1.4958; (D) composite refractive index of bases in the 276° zone, 1.5119; (E) composite refractive index of residual bases after withdrawal of A, B and C, 1.5008. The low refractive index of B is in line with the fact that this product is undoubtedly hydroaromatic, and the composite refractive index of the residual bases, lying only slightly above that of C, indicates these in the main to be hydroaromatic.

Preparation of **2,3,8-Trimethylquinoline** from its **Picrate and** Sulfate.—When either the picrate or sulfate is heated with ammonium hydroxide, the base separates as an oil which later solidifies. This is taken up with ether, the ethereal layer washed with water and the ether allowed to evaporate. Recrystallized from 50% alcohol, the

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[21] By W. A. King and J. R. Bailey.

new product separates in lustrous, rectangular plates without end faces, melts sharply at 55–56° and boils with partial decomposition at 280° (747 mm.). Characteristic of this substance is its faint fecal odor. It is readily soluble in the common organic solvents, very difficultly soluble in water even at boiling temperature and volatile with steam.

Anal. Calcd. for $C_{12}H_{13}N$: C, 84.21; H, 7.60; N, 8.19. Found: C, 84.25; 7.59; N, 8.11.

Synthesis of **2,3,8-Trimethylquinoline.**—Through the use of o-toluidine and tiglic aldehyde in the process employed by *G.* Rohde for the synthesis of 2,3-dimethylquinoline,[16] 2,3,8-trimethylquinoline was obtained in a yield of about 10%. The synthetic product, as well as numerous derivatives, was compared with the $C_{12}H_{13}N$ kerosene base and corresponding derivatives, with the result that identity of the products was confirmed in each case.

Anal. Calcd. for $C_{12}H_{13}N$: N, 8.19. Found: N, 8.07.

Sulfate, $C_{12}H_{13}N{\cdot}H_2SO_4$.—After the base, dissolved in a little more than the calculated amount of 50% sulfuric acid, separates as sulfate, the salt is filtered, washed with alcohol and recrystallized from 95% alcohol in prisms with dome-shaped end faces. The sulfate can also be prepared directly from fractions containing appreciable amounts of 2,3,8-trimethylquinoline. It decomposes around 275".

Anal. Calcd. for $C_{12}H_{15}O_4NS$: C, 53.53; H, 5.58; N, 5.20; S, 11.89. Found: C, 53.13; H, 5.87; N, 5.52; S, 11.90.

Hydrochloride, $C_{12}H_{13}N{\cdot}HCl$.—This salt is prepared by dissolving the base in 18% hydrochloric acid, from which it separates on cooling. Recrystallized from either water or alcohol, it is obtained in long, slender needles, which on heating blacken around 230" and at 260" completely decomposes without leaving a residue.

Anal. Calcd. for $C_{12}H_{14}HCl$: N, 6.75; Cl, 17.11. Found: N, 6.53; Cl, 17.03.

Nitrate, $C_{12}H_{13}N{\cdot}HNO_3$.—The base is dissolved in a slight excess of concentrated nitric acid diluted to twice the original volume, then alcohol added, and the salt precipitated with ether. On recrystallization from 95% alcohol, the nitrate separates in radiating clusters of fine needles, melting at 160.5' with gas evolution.

Anal. Calcd. for $C_{12}H_{14}O_3N_2$: N, 11.96. Found: N, 12.24.

Picrate, $C_{12}H_{13}N{\cdot}C_6H_3O_7N_3$.—Because of its difficult solubility in all the common solvents, this salt, like the sulfate, can be employed in estimating the amount of 2,3,8-trimethylquinoline in different fractions of the kerosene bases. Dissolved in hot glacial acetic acid, it separates on cooling in arborescent, canary-yellow crystals, which blacken and decompose with gas evolution at 242–245°. On heating in ammonium hydroxide solution, the base is liberated.

Anal. Calcd. for $C_{18}H_{16}O_7N_4$: C, 54.00; H, 4.00; N, 14.00. Found: C, 54.20; H, 4.24; N, 13.96.

The following characteristic salts of*2,3,8-trimethylquinoline, which were prepared but not analyzed, can be obtained from a hydrochloric acid solution of the base: gold chloride gives a salt of a yellow color, resembling the picrate and recrystallizing from water in long, slender rods; platinum chloride forms a granular, light orange-colored salt, difficultly soluble in water and alcohol; potassium dichromate gives an orange-yellow salt, best recrystallized from water in a fine, granular condition; potassium ferrocyanide precipitates the difficultly soluble hydroferrocyanide. of a light cream color, which in boiling water decomposes with evolution of prussic acid; zinc chloride gives a salt, recrystallizing from alcohol in long, slender prisms; the mercuric chloride salt is readily soluble in hot water and hot alcohol and separates from either solvent in long, slender rods; the stannous chloride salt has solubilities similar to the mercuric chloride salt and is best recrystallized from glacial acetic acid in the form of rods.

Action of Benzaldehyde on **2,3,8-Trimethylquinoline.**—The base (1 g.), benzaldehyde (1.5 g.) and zinc chloride (0.08 g.) are heated in a sealed tube at 130° for four hours, at the end of which time the contents of the tube solidify on cooling. This material is treated with ether and dilute sulfuric acid, producing separation of a deep yellow product which, when purified by recrystallization from alcohol, is obtained in sheaves of slender prisms. This substance is difficultly soluble in the common solvents other than alcohol and, on heating, begins to sinter around 198°, decomposing completely at 205°. The analysis indicates a dibenzal compound of trimethylquinoline, differing markedly in physical properties from the corresponding dibenzal-2,4,6-trimethylquinoline.[22]

Anal. Calcd. for $C_{26}H_{21}N$: N, 4.03. Found: N, 4 30.

3,8-Dimethyl-2-styrylquinoline.—The dibenzal compound described above, on dissolving in hot glacial acetic acid and precipitating with water, is changed to a light cream-colored substance, crystallizing from alcohol in sheaves of short, fine needles melting undecomposed at 120°. This product, unlike the dibenzal compound, is readily soluble in cold ether and benzene and resembles in its properties the monobenzal compound of 2,4,6-trimethylquinoline.

Anal. Calcd. for $C_{19}H_{17}N$: N, 5.41. Found: N, 5.36.

3,8-Dimethyl-2-dimethylolmethylquinoline.—In conformity with the procedure of Koenigs and Stockhausen,[23] 1 g. of the trimethylquinoline is heated with 5 cc. of 40% formaldehyde in a sealed tube for seven hours, whereby complete solution of the original base is effected. Upon dilution of the mixture to twice its volume, the reaction product separates as an oil, which is ethered out. The ether solution is then transferred to an evaporating dish, and after removal of the ether the residue is made to crystallize by protracted digestion with water on a boiling water-bath.

Another satisfactory method of isolation of the formaldehyde compound is precipitation as picrate by the addition of one mole of picric acid in hot alcohol to its ethereal solution. The picrate is decomposed with ammonium hydroxide and the base extracted with ether. For purification the product is recrystallized from ether or acetic ether in long, slender prisms with well-defined end faces. It is readily soluble in alcohol, difficultly soluble in water, melts at 111.5° and boils at 170–172° (3 mm.).

Anal. Calcd. for $C_{14}H_{17}O_2N$: C, 72.73; H, 7 36; N, 6.06. Found: C, 72.79; H, 7.45; N, 6.13.

Picrate of 3,8-Dimethyl-2-dimethylolmethylquinoline.—This characteristic salt is readily soluble in alcohol and more difficultly soluble in acetic ether and water, crystallizing from all these solvents in rods of a light orange color. It melts at 180°, apparently undecomposed.

Anal. Calcd. for $C_{20}H_{20}O_9N_4$: C, 52.17; H, 4.35; N, 12.17. Found: C, 52.17; H, 4.39; N, 12.20.

3,8-Dimethylquinoline-2-carboxylic Acid.—To 10 g. of the formaldehyde compound in 200 cc. of acetone and 10 cc. of glacial acetic acid is added in small portions with cooling 41 3 g. of finely ground potassium permanganate. The sludge containing the potassium salt of the oxidation product is filtered off, the cake extracted with hot water and the dimethylquinolinic acid precipitated with hydrochloric acid. For purification it is dissolved in ammonium hydroxide, decolorized with filt-char, and precipitated with hydrochloric acid. Finally the product is dissolved in boiling glacial

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[22] Fischer, Müller and Merkel, *J. prakt. Chem.*, **100**, 100 (1919).

[23] Wilhelm Koenigs and Ferdinand Stockhausen, Ber., 34, 4331 (1901).

acetic acid, water added to turbidity and the solution treated with filt-char. From alcohol the acid separates in long, slender prisms and from water in fine needles, melting with decomposition at 157.5'. Boiled in water with calcium carbonate, it forms a readily soluble salt which gives gelatinous precipitates with soluble salts of silver, copper and lead. Permanganate oxidation gives a 50% yield of the dimethylquinolinic acid. After several failures to employ nitric acid successfully in oxidation of the formaldehyde compound, the following conditions were found to give a 95% yield of crude dimethylquinolinic acid: one g. of the formaldehyde compound is warmed with a mixture of 25 cc. of concentrated nitric acid and 25 cc. of water until the copious evolution of nitrous fumes ceases, and then the mixture is heated to boiling for four hours. The nitric acid is neutralized with sodium hydroxide to the point where a precipitate begins to form, when, on addition of several grams of sodium acetate, the dimethylquinolinic acid separates. A small amount remaining in solution can be extracted with chloroform.

Anal. Calcd. for $C_{12}H_{11}O_2N$: N, 6.97. Found: N, 7.01.

3,8-Dimethyl-2-hydroxyethylquinoline.—In the oxidation of the formaldehyde compound in acetone without the presence of acetic acid only a 17% yield of the dimethylquinolinic acid was obtained. Considerable amounts of the by-products of the oxidation remained in the acetone. On distillation the acetone residue yielded at first an oil and then a solid base. Of these two products only the latter was investigated. It was purified by crystallization from petroleum ether, followed by a second distillation. The product is readily soluble in the common organic solvents, crystallizes from petroleum ether in an arborescent, granular form and melts at 99°. This product is of interest, because it indicates that in one stage of the oxidation one mole of formaldehyde is eliminated and the $—CH(CH_2OH)_2$ complex converted to $—CH_2CH_2OH$. It gives a beautifully crystallizing picrate which separates from alcohol in long, slender prisms, melting with decomposition at 162°.

Anal. Calcd. for $C_{13}H_{15}ON$: N, 6.97. Found: N, 6.91.

Anal. of picrate. Calcd. for $C_{19}H_{18}O_8N_4$: N, 13.02. Found: N, 13.26.

3,8-Dimethylquinoline from **3,8-Dimethylquinoline-2-carboxylic** Acid.—The dimethylquinolinic acid on distillation with four times its weight of soda lime is converted to a new base of the formula $C_{11}H_{11}N$, the structure of which was established as 3,8-dimethylquinoline by synthesis. It has a faint quinoline odor and possesses the following physical constants: b. p. (751 mm.) 269"; d_{20}^{20} 1.051; n_D^{20} 1.6063.

Anal. Calcd. for $C_{11}H_{11}N$: N, 8.92. Found: N, 9.16.

Synthesis **of 3,8-Dimethylquinoline.**—A moderate stream of dry hydrogen chloride gas is led into a mixture of propionic aldehyde (30 g.) and methylal (39.3 g.) for five minutes. On addition of this mixture to o-toluidine (42 g.) and concentrated hydrochloric acid (72 g.), the reaction begins and is completed by gently boiling the solution for three hours. The reaction mixture is then added to an equal volume of water and, after filtration, treated with a slight excess of sodium nitrite. The filtered solution is finally concentrated to a small volume, the bases liberated with sodium hydroxide and, after extraction with ether, the mixture fractionated in a vacuum. Further purification of the dimethylquinoline, obtained in a yield of about 7%, is effected through the picrate. On crystallization by-product picrates first separate and are discarded. For comparison the following salts were made of both the synthetic base and the base prepared from 2,3,8-trimethylquinoline in the series of reactions described above. The sample of synthesized base analyzed had a refractive index, n_D^{20} 1.6069.

Anal. Calcd. for $C_{11}H_{11}N$: N, 8.92. Found: N, 8.98.

Picrate.—This salt is readily soluble in glacial acetic acid and difficultly soluble in alcohol and water. It crystallizes from acetic acid in thin prismatic plates and from water in needles which under the microscope appear as long slender prisms. It melts at 207° with decomposition.

Anal. Calcd. for $C_{17}H_{14}O_7N_4$: N, 14.51. Found: N, 14.73.

Picrolonate.—This salt crystallizes from alcohol in a form similar to the picrate and melts with decomposition at 199°.

Anal. Calcd. for $C_{21}H_{19}O_5N_5$: N, 16.63. Found: N, 16.79.

1,2,3-Trimethylquinolinium Iodide.—Methyl iodide reacts with 3,8-dimethylquinoline in a sealed tube at water-bath temperature, giving a product that crystallizes from alcohol in long, thin, slender prisms melting at 197°.

Anal. Calcd. for $C_{12}H_{14}NI$: N, 4.68. Found: N, 4.71

Oxalate.—The base with oxalic acid in absolute alcohol separates the oxalate in long slender prisms melting at 128°.

Anal. Calcd. for $C_{13}H_{13}O_4N$: N, 5.66. Found: N, 5.43.

2,3-Dimethylquinoline-8-carboxylic Acid.—2,3,8-Trimethylquinoline (11.5 g.) is boiled for thirty hours with 23 g. of chromic anhydride in 100 cc. of 1:5 sulfuric acid. The dimethylquinolinic acid in a yield of about 16% can be extracted with chloroform, after the oxidation mixture is neutralized with ammonium hydroxide to the point where chromic hydroxide begins to precipitate. With this oxidation product removed, a considerable amount of unchanged trimethylquinoline can be regained by addition of ammonium hydroxide in excess. The dimethylquinolinic acid is purified by recrystallization from alcohol and finally from water with the addition of filt-char. It separates from benzene, acetic ether, alcohol and water in long needles, melting apparently undecomposed at 202°.

Anal. Calcd. for $C_{12}H_{11}O_2N$: N, 6.97. Found: N, 7.05.

2,3-Dimethylquinoline.—Soda lime distillation converts the acid just described to a base of the formula $C_{11}H_{11}N$, from which, after distillation, a small amount of liquid impurity can be absorbed on porous plate. Only a few of the known dimethylquinolines are solids at room temperature, and of these the 2,3-dimethyl isomer has the highest melting point, 67.5–69°. The identity of our product with 2,3-dimethylquinoline, synthesized from o-aminobenzaldehyde and methyl ethyl ketone, was established in the usual way, and further confirmed by a comparison of the picrate made from the two samples of base.[24]

Anal. of base. Calcd. for $C_{11}H_{11}N$: N, 8.92. Found: N, 8.99.
Anal. of picrate. Calcd. for $C_{17}H_{14}O_7N_4$: N, 14.51. Found: N, 14.62.

Summary

1. The preparation of 50 liters of bases from 150 barrels of residues obtained in refining California crude kerosene distillate is described.

2. A figure of the distillation apparatus employed in rectifying the bases is given.

3. The separation of the bases into approximately fifty fractions, with a boiling-point range of 180 to 335°, by repeated fractional distillation at reduced pressures is outlined.

4. The different methods being employed in isolation of the component bases in the distillation fractions in the 276° zone (atmospheric pressure) are discussed.

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[24] J. Eliasberg and P. Friedlander, *Ber.*, 25,1754 (1892).

5. The structure of a base occurring in California kerosene stock as 2,3,8-trimethylquinoline is established, and its synthesis effected.

6. The preparation of 3,s-dimethyl- from 2,3,8-trimethylquinoline through a series of reactions, with the structure of the 3,8-dimethylquinoline confirmed by synthesis, is described.

7. This investigation reveals in Edeleanu residues from refining California crude petroleum distillate a vast wealth of nitrogen bases, probably in the main hydro-aromatic and in *greater amount* volatile, non-basic nitrogen compounds. For the separation of the latter methods remain to be developed. Although there is a practically inexhaustible potential supply of material for research in this field, anything like an intensive investigation of petroleum nitrogen will involve a great amount of labor and expense.

AUSTIN, TEXAS

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

THE PREPARATION OF SEMICARBAZIDE

BY L. F. AUDRIETH

RECEIVED NOVEMBER 18, 1929 PUBLISHED MARCH 6, 1930

Semicarbazide in the form of its compounds has been used extensively in various organic reactions, but no simple method for the preparation of the free base has, as yet, been reported in the literature. The action of liquid ammonia upon certain hydrazine[1] and hydroxylamine[2] salts, in particular the sulfates, has afforded a convenient and expeditious means for the preparation of these bases, suggesting that this reaction might also be applied to semicarbazide. It was found that semicarbazide sulfate would react with liquid ammonia to give the free base in excellent yields. This method is both rapid and convenient and one which is highly desirable in view of the fact that semicarbazide undergoes decomposition rapidly and must, therefore, be prepared fresh. The reaction proceeds in accordance with the equation

$$NH_2CON_2H_3\cdot H_2SO_4 + 2NH_3 = NH_2CON_2H_3 + (NH_4)_2SO_4$$

The ammonium sulfate settles out as an insoluble precipitate from which the liquid ammonia solution of semicarbazide may readily be decanted. The ammonia may be removed by evaporation and the semicarbazide purified by recrystallization from absolute ethanol.

An alternative method employed by the author for preparing the free base involves the action of barium hydroxide upon the sulfate. An excess of barium hydroxide must be avoided since alkalies induce hydrolysis of semicarbazide. After removal of the precipitated barium sulfate, the

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[1] Browne and Welsh, THIS JOURNAL, 33, 1728 (1911).

[2] Browne and Audrieth, unpublished investigations.

filtrate is concentrated by vacuum evaporation at temperatures below 60°. Evaporation of an aqueous solution of semicarbazide at the boiling point under ordinary atmospheric pressure results in a decided decrease in yields due to decomposition of the substance with formation of hydrazine and hydrazidicarbamide.[3]

Of the new methods outlined above for the preparation of semicarbazide from its sulfate, the first is much to be preferred since it is not only faster, but gives much better yields. Attempts to prepare free guanidine and aminoguanidine by treatment of the corresponding sulfates with liquid ammonia were unsuccessful, suggesting that possibly only those anhydrobases less basic than ammonia are susceptible to ammonolysis. Treatment of methylhydrazine sulfate with liquid ammonia has been employed by the author for the preparation of liquid ammonia solutions of methylhydrazine, although examination of the residues indicates that this reaction does not go to completion.

Experimental

Preparation of Semicarbazide by Ammonolysis of Semicarbazide Sulfate.—Five grams of the sulfate was added gradually to 40 cc. of liquid ammonia. The solution was agitated for a short time and the precipitate then allowed to settle. The clear supernatant liquid was removed by decantation and the residue washed with additional liquid ammonia. Upon evaporation of the ammonia, the solid residue was dissolved in hot absolute ethanol, which on cooling yielded 2 g. of semicarbazide, m. p. 96°, corresponding to a 93% yield.

Preparation of Semicarbazide by Treatment of the Sulfate with Barium Hydroxide.—A concentrated solution of the sulfate (17.3 g.) was treated with an aqueous solution of barium hydroxide and the excess of the latter removed by the addition of the requisite amount of dilute sulfuric acid. After removal of the precipitated barium sulfate, the solution was concentrated at reduced pressure below 60° and the crystalline residue extracted with hot ethanol. Six grams of the free base, corresponding to an 80% yield, was obtained.

Summary

Free semicarbazide may be prepared rapidly and conveniently by the ammonolysis of semicarbazide sulfate. An alternative method involves the action of barium hydroxide upon the same salt.

URBANA, ILLINOIS

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[3] Curtius and Heidenreich, Ber., 27, 57 (1894).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE CHEMISTRY OF THE LIPOIDS OF TUBERCLE BACILLI. XIII. THE OCCURRENCE OF MANNOSE IN THE PHOSPHATIDE FROM HUMAN TUBERCLE BACILLI[1]

BY R. J. ANDERSON AND A. G. RENFREW[2]

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Introduction

In a study of the cleavage products of the phosphatide fraction[3] isolated from the human type of tubercle bacilli, strain H-37, it was found that the water-soluble constituents amounted to about 33%. The aqueous solution contained reducing sugars, glycerophosphoric acid and some substance which formed a crystalline derivative with phenylhydrazine. These products were separated by first precipitating the glycerophosphoric acid as the barium salt with alcohol. After removal of the excess of barium with sulfuric acid, the concentrated solution was mixed with phenylhydrazine, when a crystalline derivative separated and was filtered off. The filtrate on treatment with phenylhydrazine hydrochloride and sodium acetate yielded typical glucosazone crystals. In addition to the three components mentioned above, a small quantity of another crystalline compound was isolated from the residual sirup but this substance has not yet been identified.

The crystalline phenylhydrazine compound was regarded as a salt of some sugar acid but owing to stress of other work it was impossible at that time to analyze or identify the substance. Recently we have had an opportunity to resume the investigation of the compound and we have come to the conclusion that it is not a salt of a sugar acid but that it is mannose phenylhydrazone.

The identification was accomplished by comparing the properties of the purified substance with those of pure mannose phenylhydrazone. Both substances formed colorless crystals that melted with decomposition at 195° and a mixed melting point showed no depression. Examination of the optical properties of the two crystals also showed that they were identical.

Since a considerable amount of glucosazone could be isolated from the original hydrolysis mixture after removing the insoluble mannose phenylhydrazone, it is evident that the carbohydrate complex contained in the phosphatide yields on hydrolysis at least two reducing sugars, *viz.*, mannose arid probably glucose, and in addition some other as yet unidentified sub-

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[1] The present report is a part of a cooperative investigation on tuberculosis; it has been supported partly by funds provided by the Research Committee of the National Tuberculosis Association.

[2] Holder of a National Tuberculosis Association Fellowship at Yale University, 1929–1930.

[3] R. J. Anderson, J. *Biol.* Chem., **74, 537 (1927).**

stance is present which crystallizes rather easily from a concentrated aqueous solution.

Experimental Part

The crude phenylhydrazone had been obtained as already described.[3] The individual crystals appeared to be colorless but in bulk they exhibited a yellowish color. The crystals were almost insoluble in alcohol and very slightly soluble in hot water. The substance dissolved slowly in boiling water but the color became deep yellow and on cooling large brownish-yellow crystals separated. The crude crystals melted with decomposition at 194–195°.

For purification, 0.6 g. of the crystals was dissolved in 60 cc. of hot 60% alcohol, giving a slightly yellowish solution. Dense colorless plate-shaped crystals separated slowly after the solution had cooled. The crystals were filtered off and washed with alcohol, acetone and ether. After the crystals had been dried *in vacuo* over sulfuric acid, they weighed 0.5 g.

A sample of mannose phenylhydrazone was prepared as follows: 4 g. of crude mannose[4] prepared from the ivory nut was dissolved in 25 cc. of water, treated with norite and filtered. The clear filtrate was mixed with a slight excess of phenylhydrazine dissolved in a little alcohol. The hydrazone soon began to crystallize and after the mixture had stood overnight the crystals were filtered off and washed with water and with alcohol. The product was recrystallized from 350 cc. of hot 60% alcohol, yielding about 3 g. of large colorless plate-shaped crystals.

In crystal form and in solubilities the two products mentioned above appeared to be identical. Both substances melted with decomposition at the same temperature but the melting point varied considerably depending upon the rate of heating. When heated with moderate rapidity the melting point was 195–196°. When the rate of heating was more rapid, the melting point was 197–198° and in another case 204–205°. A mixture of the two products melted at the same temperature; the capillary tubes were attached to the same thermometer and heated simultaneously.

The nitrogen content of the crystals isolated from the phosphatide corresponded to that of a hexose phenylhydrazone.

Anal. Subs., 0.1837: 16.90 cc. of N_2 at 22° and 763 mm. Calcd. for $C_{12}H_{18}O_5N_2$ (270): N. 10.37. Found: N, 10.64.

Mannose phenylhydrazone according to Hoffmann[5] shows in pyridine solution a specific optical rotation of about $+27°$, while Levene and Mori[6] report a specific rotation of $+32.5°$ for a solution of the substance in 50% pyridine and water. We were unable to determine the optical rotation with any satisfactory degree of accuracy because both preparations were so slightly soluble in pyridine or in a 50% mixture of pyridine and water that prolonged warming was necessary before 0.2 or 0.1 g. of substance could be dissolved in 25 cc. of the solvent. The solutions which were obtained turned decidedly yellow in color during the warming and we were unable to make any accurate readings.

The optical properties of the crystals obtained from the phosphatide

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[4] We are indebted to Dr. R. H. F. Manske of this Laboratory for kindly supplying the mannose.

[5] A. Hoffmann, *Ann.*, 366, 277 (1909).

[6] P. A. Levene and T. Mori, *J. Biol. Chem.*, 84, 49 (1929).

were compared with those of pure mannose phenylhydrazone by Dr. E. J. Roberts of this Laboratory and the two crystals were found to be identical. The results of the examination are stated by Dr. Roberts as follows. "Mannose phenylhydrazone crystallizes in the form of rhombic plates which are biaxial positive with $2V \doteqdot 75°$; $\beta = 1.65$, $\alpha = 1.60$, $\gamma \doteqdot 1.74$. Most of the plates show an *almost* perpendicular emergence of an optic axis, have an acute angle of 75° and an extinction angle of 23° in the acute angle. The trace of the axial plane passes through the acute angle of the rhomb. The crystals obtained from the phosphatide have identical properties."

Summary

One of the reducing sugars formed on hydrolyzing the phosphatide isolated from the human tubercle bacillus has been identified as mannose.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION NO. 24 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY]

THE THERMAL DECOMPOSITION OF SODIUM AND POTASSIUM METHIDES

BY WALLACE H. CAROTHERS AND DONALD D. COFFMAN

RECEIVED NOVEMBER 22, 1929 PUBLISHED MARCH 6, 1930

In a previous paper[1] the results of a study of the thermal decomposition of sodium methide were reported.

The thermal decompositions of sodium and potassium methides have now been studied and found to proceed in accordance with Equation 1.

$$8MCH_3 \longrightarrow 6CH_4 + M_2C_2 + 6M \quad (M{=}Na, K) \qquad (1)$$

Pure methane is liberated in the calculated amount and, on treatment of the residue with water, the rest of the carbon is set free as acetylene mixed with ethylene and ethane.[2]

Sodium and potassium methides are primary salts of the very weak volatile polybasic acid, methane. When salts of this general class are heated the usual result is the liberation of free acid and the formation of a new salt in which all the available hydrogens of the residual acid have been replaced. This process consists in the displacement of a prototropic equilibrium[3] by the constant removal of one of the participating entities. In accordance with this general behavior is the liberation of methane from sodium or potassium methide

$$4CH_3^- \longrightarrow 3CH_4 + C^{----} \qquad (2)$$

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[1] Carothers and Coffman, THIS JOURNAL, 51, 588 (1929).

[2] The presence of ethylene and ethane may be ascribed to the fact that the acetylene is formed under powerfully reducing conditions (action of water on excess sodium or potassium).

[3] Lowry, *Institute International de Chemie Solvay, 2,* 150 (1926).

Each of three methide ions captures a proton from a fourth ion, and the latter should, therefore, appear in the residue as the tetravalent methide anion. This, however, does not persist, for what is actually found in the residue is the acetylide ion, Electrons must, therefore, have been liberated (to sodium or potassium cations) and new covalent bonds established

$$2C^{----} \longrightarrow C\equiv C^{--} + 6\,\ominus \tag{3}$$

This union of the carbons must have occurred after they were completely stripped of their protons, since if it had occurred at any earlier stage, less than the calculated amount of methane would have been formed; moreover, hydrogen would then have appeared in the gas or sodium hydride in the residue.

The rather unusual reaction represented by Equation 3 may be regarded as an expression of carbon's very limited tolerance for a free electron pair, a property which is manifested in practically all the reactions of the alkali alkyls. The transformations of these extraordinarily reactive compounds almost invariably lead to the disappearance of the free electron pair either by sharing or by surrender. Thus, at 100° the ethide anion, $CH_3CH_2^-$, (in sodium ethide)[4] discards its free pair and, no more readily reducible substance than sodium ion being present to accept these electrons, a proton is lost with them, so that they appear as hydride ion. This permits the establishment of a new covalent bond between the two carbon atoms,[5] and ethylene[6] is formed. In the tetravalent methide ion this tendency to discard the free electron pairs is so great as to bring about the reduction of sodium and potassium ions to the free metals. The experiments here described do not prove that the tetravalent methide ion is incapable of existence; they merely indicate that at 250° its life must be very brief.

The thermal decomposition of magnesium methyl iodide has already been studied by Jolibois[7] with results in part similar to those recorded above. Four moles of CH_3MgI yielded three of methane. The residue, which appeared to be a mixture of $Mg_2C{\cdot}MgI_2$ and MgI_2 (from which the latter could be extracted with ether), reacted very violently with water at ordinary temperature with the liberation of gas composed of varying propor-

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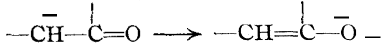
[4] Carothers and Coffman, THIS JOURNAL, 51, 508 (1929).

[5] The analogy with the transformation  $-\overset{-}{C}H-\overset{|}{C}=O \longrightarrow -CH=\overset{|}{C}-\overset{-}{O}-$ is obvious. Here the free electron pair is lost in effect to the oxygen atom, and a comparison of the probabilities of the first and second states may be found in the relative tendencies of hydrogen ion and oxygen atom to accept an electron pair.

[6] But to represent this (as is sometimes done) as permanently existing in the active form, $CH_2^+-CH_2^-$, which would be the immediate result of the steps indicated above, would be to ignore the forces responsible for its formation. There is no reason to suppose that the free pair would be more readily tolerated in such an active form than it is in the ethide ion, and this improbable situation can be corrected by the immediate establishment of the new covalent bond.

[7] Jolibois, *Compt.* rend., 156, 712 (1913).

tions of acetylene, ethylene and saturated hydrocarbons. When he carried out the reaction as slowly as possible by introducing moist ether at −80°, the evolved gas consisted of ethylene 3% and methane 97%. In view of these results we suspected that Na_4C and K_4C might actually be present in the residues from the thermolysis of the corresponding methides, and that the liberation of acetylene might be due to a catalytic transformation of Na_4C into Na_2C_2 under the influence of water. But when the water was introduced into the reaction tube at −80° and the action regulated by allowing the temperature to rise very slowly, the gas, as before, consisted of acetylene and ethylene together with a small amount of saturated hydrocarbon which may have been methane but which we assumed to be ethane.

Jolibois reports that the thermal decomposition of methylmagnesium iodide occurs at 240°. Under the conditions of our experiments the decompositions of sodium and potassium methides began very slowly at room temperature. The decomposition of sodium methide became quite rapid at about 200° and could be completed at a slightly higher temperature. The residual carbon present as sodium acetylide and representing 25% of the total was not liberated by heating to the softening point of pyrex glass. The thermal decomposition of potassium methide began at a much lower temperature—it was quite appreciable at 50° and rapid at 100°, but evolution of gas at this temperature ceased before decomposition was complete; on raising the temperature, gas was again evolved, but not until the temperature reached 240° did the evolution again become rapid. The gas consisted entirely of methane.

The compounds K_2CH_2 and K_3CH would naturally be intermediate in the passage from KCH_3 to K_4C, and the stepwise evolution of gas indicated that one of these intermediates has a higher thermal stability than KCH_3. In one experiment the amount of gas evolved below 203° was found to be about twice that evolved above 203°, as would be required if K_2CH_2 were an intermediate stable below that temperature.

$$8KCH_3 \longrightarrow 4CH_4 + 4K_2CH_2 \qquad (4)$$

$$4K_2CH_2 \longrightarrow 2CH_4 + K_2C_2 + 6K \qquad (5)$$

Attempts to prove the presence of K_2CH_2 by interrupting the thermolysis after the first stage and treating the residue with phenyl isocyanate or with carbon dioxide were unsuccessful. Moreover, the methane formed by treating this residue with water was contaminated with acetylene, and this indicated at least a partial overlapping of the steps. Nevertheless, we are still inclined to assume the intervention of K_2CH_2 and to ascribe some degree of stability to it, since it is otherwise difficult to explain the stepwise evolution of methane.

Experimental Part

The technique used in the preparation of sodium and potassium methides and in effecting their decomposition was the same as that previously described for sodium ethide.[1] Mercury methyl appears to react more rapidly with sodium than does mercury ethyl. The methides were not isolated as such; the decomposition was carried out directly on the mixture of metallic alkyl, alkali metal and mercury which resulted from the action of dimethyl mercury on the alkali metal.

Thermal **Decomposition** of **Sodium Methide**

Experiment 2.--Sodium methide was prepared from 1.052 g. of mercury methyl and 1 g. of sodium. The reaction between the mercury methyl and sodium appeared to be complete in three hours. After twenty-four hours the thermal decomposition was started. The rate of decomposition became appreciable at about 120° and rapid at 200". The temperature of the heating bath was carried up to 268°; gas collected, 146.5 cc. (Fraction A). The residue was heated to the softening point of pyrex glass; gas collected, 15.0 cc. (Fraction B).

Analysis of Fraction A (by explosion): CH_4 (by contraction), 100.65; CH_4 (by absorption), 101.1; C/A, 1.99.[8]

Analysis of Fraction B (by explosion): CH_4 (by absorption), 60.9; H_2 (by contraction), 40.25; total, 101.1.

Thus from one mole of sodium methide there was evolved 0.715 mole of methane in Fraction A, and 0.0444 mole in Fraction B. The total (0.759 mole) is 101% of that required by Equation 3. The small amount of hydrogen (0.029 mole) formed at the higher temperatures was probably due to the liberation of water from the walls of the glass.

The action of absolute alcohol on the residue from the thermal decomposition led to the evolution of 51.6 cc. of gas which gave a positive qualitative test for acetylene

Anal. (by explosion): C_2H_2 (by absorption), 56.43; H_2 (by contraction), 43.67; total, 100.1.

In this analysis all of the carbon is assumed to be present as acetylene, and calculation indicates 29.2 cc., while Equation 3 requires 25.6 cc.

Experiment 3.—Sodium methide prepared from 1.249 g. of mercury methyl and 0.5 g. of sodium was decomposed by heating slowly to 225°. One hundred and seventy-nine cubic centimeters of gas was evolved (Fraction A). Treatment of the residue with absolute ethyl alcohol at room temperature yielded 69.8 cc. of gas (Fraction B).

Analysis of Fraction A (by explosion): CH_4 (by contraction), 99.8; CH_4 (by absorption), 102.1; C/A, 1.95.

This fraction was, therefore, methane and its amount was 98% of that required by Equation 1.

Analysis of Fraction *B* (by explosion): C_2H_2, 46.32; (by absorption with ammoniacal silver nitrate solution and with potassium mercuri-iodide), C_2H_2, 33.13; C_2H_4 (by absorption with bromine water), 11.54; C_2H_6 (by explosion and absorption), 1.61; H_2 (by contraction), 35.64.

Thus Fraction B contained a total of 32.35 cc. of acetylene, ethylene and ethane, while the theoretical is 30.6 cc. The saturated gas calculated as ethane may have been methane, but it represented only a small fraction of the total.

Experiment 4.—From 1.057 g. of mercury methyl and 0.5 g. of sodium there was obtained by thermal decomposition 150 cc. of methane or 97% of the calculated amount.

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[8] $C/A = \frac{\text{Contraction due to combustion}}{\text{Contraction due to absorption}} = \frac{H_2O\text{ formed.}}{CO_2\text{ formed}}$ Calcd. for methane 2.00.

The vessel containing the residue was cooled to −80°, and water was allowed to distil into it slowly, the whoie system being completely evacuated. The temperature of the residue was allowed to rise very slowly to 25°. Two fractions of gas were collected. The first (Fraction A) had a volume of 97 cc.; the second (Fraction B) had a volume of 102 cc.

Analysis of Fraction *A:* C_2H_2 (by absorption with ammoniacal silver nitrate solution), 16.89; C_2H_4 (by absorption with bromine water), 3.04; C_2H_6 (by explosion and absorption), 1.64; H_2 (by contraction), 75.01.

Analysis of Fraction B: C_2H_2 (by absorption with ammoniacal silver solution), 2.17; C_2H_4 (by absorption with bromine water), 3.00; C_2H_6 (by explosion and absorption), 3.97; H_2 (by contraction), 84.77.

The total of the acetylene, ethylene and ethane in the two fractions amounts to 30.2 cc., while the theoretical is 25.7 cc. The saturated hydrocarbon amounting to 18.3% of this total is assumed to be ethane, and in accordance with this assumption its relative amount in Fraction A is much smaller than in Fraction B, while if it were methane originating from Na_4C, the reverse should be true.

Thermal Decomposition of Potassium Methide

Experiment 2.—Potassium methide formed by the action of 0.809 *g.* of mercury methyl on 0.5 g. of potassium was decomposed. The evolution of gas (collected in two fractions) commenced in the neighborhood of 50° and terminated at a temperature somewhat below 300°: Fraction **A,** 63 cc.; Fraction B, 55.8 cc.; total, 118.8 cc., or 100.8% of the calculated amount.

Analysis of Fraction *A* (by explosion): CH_4 (by contraction), 100.8; CH_4 (by absorption), 104.4; *C/A,* 1.93.

Analysis of Fraction B (by explosion): CH_4 (by contraction), 101.4; CH_4 (by absorption), 102.8; *C/A,* 1.97.

The residue on treatment with water yielded acetylene and hydrogen together with some ethylene and a saturated gas assumed to be ethane.

Experiment 3.—Potassium methide formed from 0.831 g. of mercury methyl and *0.5* g. of potassium was decomposed. The gas was collected in three fractions.

FRACTION **A,** 23.6 cc. This gas was pumped off before heating after the tube had stocd at room temperature for twenty-four hours.

Anal. (by explosion): CH_4, 89.01; C_2H_6 or $Hg(CH_3)_2$, 10.99; *C/A,* 1.82.

The second gas was probably dimethyl mercury, since the characteristic odor of that substance was present; and, in the calculation of yield, correction was made for this loss.

FRACTION B, 52.7 cc. This fraction was evolved between 25 and 203°, most of it between 50 and 103° in one hour.

Anal. (by explosion): CH_4 (by contraction), 99.8; CH_4 (by absorption), 102.4; *C/A,* 1.94.

FRACTION C. Pumping was continued while the residue remained at 203° for one and one-half hours. Only a minute amount of gas was collected at this temperature. The temperature was then allowed to rise. Between 204 and 280°, 39 cc. of gas was collected in one hour.

Anal. (by explosion): CH_4 (by contraction), 100; CH_4 (by absorption), 103.2, *C/A,* 1.94

The ratio of methane in Fractions A and B to that in C is 1.89:1, in fair agreement with the requirements of Equations 4 and 5.

Summary

On heating sodium or potassium methide, methane is evolved in accordance with the equation $4MCH_3 \rightarrow 3CH_4 + M_4C$. Hydrolysis of the residue yields chiefly acetylene and hydrogen, together with some ethylene and ethane, indicating the transformation $2M_4C \rightarrow M_2C_2 + 6M$. The thermolysis of sodium methide becomes rapid at about 200° and may be completed at a slightly higher temperature. The thermolysis of potassium methide first becomes rapid at 100° but is not completed below 250°. In this behavior evidence is found for the intervention of K_2CH_2 or K_3CH in the passage from KCH_3 to K_4C. The mechanisms of these reactions are discussed.

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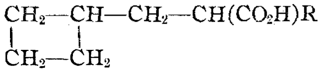
[Contribution from the Chemistry Department of the University of Illinois]

CYCLOBUTYLALKYL ALKYL ACETIC ACIDS AND THEIR BACTERICIDAL ACTION TOWARD B. LEPRAE. XVI[1]

By S. G. Ford and Roger Adams

Received November 29, 1929 Published March 6, 1930

In a number of previous papers in this series[2] it was shown that certain ω-cyclohexylalkyl, ω-cyclopentylalkyl, ω-cyclopentenylalkyl and ω-cyclopropylalkyl alkyl acetic acids were bactericidal toward B. *Leprae*. The preparation of various cyclobutylmethyl alkyl acetic acids (I) was undertaken at the same time, but owing to experimental difficulties the compounds were not completed before the interesting discovery was made that no ring structure in the molecule was necessary for bactericidal action. The research on the cyclobutyl derivatives, however, was continued and results are described in this communication. Cyclobutylmethyl alkyl acetic acids (I) were prepared in which the alkyl group was n-octyl, n-nonyl, n-decyl, n-undecyl and n-dodecyl.

(I) 

The bacteriological tests have shown that molecular weight is an important factor, as might have been anticipated from the study of the previous compounds which were prepared and tested. Those molecules which contained sixteen to eighteen carbon atoms were the most effective and gave results comparable to the other ring acids of the same molecular weight.

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[1] This communication is an abstract of a portion of a thesis submitted by S. G Ford in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Illinois.

[2] For previous articles, see paper XV of this series, Stanley, Jay and Adams, This Journal, **51**, 1261 (1929).

TABLE I

BACTERIOLOGICAL ACTION OF CYCLOBUTYL ALKYL ACETIC ACIDS TO B. *Leprae*

	Dilutions of sodium salts in thousands											
	5	25	50	62	74	85	100	125	155	192	250	333
$C_4H_7CH_2CH(CO_2H)C_8H_{17}$-*n*						±	+	+	+	+	+	+
$C_4H_7CH_2CH(CO_2H)C_9H_{19}$-*n*	–	–	–	–	–	–	–	±	±	+	+	+
$C_4H_7CH_2CH(CO_2H)C_{10}H_{21}$-*n*	–	–	–	–	–	–	–	–	±	±	+	+
$C_4H_7CH_2CH(CO_2H)C_{11}H_{23}$-*n*	–	–	–	–	–	±	±	±	+	+	+	+
$C_4H_7CH_2CH(CO_2H)C_{12}H_{25}$-*n*	–	–	+	+	+	+	+	+	+	+	+	+

The cyclobutylmethyl alkyl acetic acids were prepared through the malonic ester synthesis, by the use of cyclobutylmethyl bromide and the necessary diethyl monoalkyl malonates.

The diethyl ester of cyclobutane-1,1-dicarboxylic acid was prepared[3] and by direct reduction converted to cyclobutyl carbinol. Care had to be taken in conversion of the alcohol to the corresponding bromide. Demjanow[4] has shown that cyclobutyl carbinol when treated with hydrobromic acid rearranges to cyclopentyl bromide. A method which proved most successful for forming the bromide without rearrangement was a modification of that of Darzens,[5] in which the alcohol was treated with phosphorus tribromide in the presence of pyridine. By this procedure all free acid was avoided and the reaction ran smoothly, though with poor yields, to give cyclobutylmethyl bromide.

The authors are indebted to Dr. W. M. Stanley for carrying out the bacteriological tests.

Experimental

1,1-Dicarbo-ethoxycyclobutane.—The method of Kishner[3] was followed with success. The yield was 38% of a product boiling at 110–113° (20 mm.); n_D^{25} 1.4373; d_4^{25} 1.0445.

Cyclobutyl **Carbinol.**—A total of 365 g. of tetramethylene dicarboxylic ester was reduced to cyclobutyl carbinol in seven separate reductions by the toluene method.[6] In each experiment 52 g. of tetramethylene dicarboxylic ester, 650 cc. of absolute alcohol, 85 g. of sodium and 200 cc. of anhydrous toluene were used. After each reduction the excess ethyl alcohol was distilled off under slightly diminished pressure, two or three reduction mixtures combined, placed in a continuous extractor and extracted with ether for thirty-six hours. The ether was evaporated and the cyclobutyl carbinol distilled at atmospheric pressure. The yield was 76 g. (48.5%) of a product boiling at 140–143"; n_D^{25} 1.4449.

Cyclobutylmethyl Bromide.[7]—This was made by a modification of the method of

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[3] (a) Kishner, J. *Russ. Phys.-Chem. Soc.*, 37, 507 (1905); (b) Zelinsky, *Ber.*, 46, 1093 (1913); (c) *ibid.*, 60, 711 (1927).

[4] Demjanow, *Ber.*, 40, 4959 (1907); J. *Russ. Phys.-Chem. Soc.*, 35, 26 (1903); ibid., 42, 837 (1910).

[5] Darzens, *Compt. rend.*, 152, 1314 (1911).

[6] Stanley and Adams, THIS JOURNAL, 51, 1515 (1929).

[7] V. Braun, Fussganger and Kuhn, Ann., 445, 201 (1925), first prepared this substance by the action of phosphorus pentabromide on benzoyl cyclobutylmethyl amide.

Darzens.[5] A mixture of 59 g. of cyclobutyl carbinol, 17.5 g. of anhydrous pyridine and 50 cc. of dry ether was placed in a 200-cc., three-necked flask equipped with a stirrer, dropping funnel and a loosely-stoppered thermometer. The flask was immersed in an ice–salt bath and when the temperature of the contents of the flask had dropped to −10°, there was added with stirring a previously cooled solution of 62 g. of phosphorus tribromide in 30 cc. of absolute ether sufficiently slowly to keep the reaction mixture below −5°. After standing at 0° for two hours, the liquid was decanted from the solid material. The solid material was washed with cold anhydrous petroleum ether (25–40°) and the ether combined with the decanted liquid. The cold solution was neutralized with cold 50% potassium hydroxide solution, washed with water and the ethereal solution dried over anhydrous potassium carbonate. The ether was removed and the cyclobutylmethyl bromide was distilled under reduced pressure. The yield was 25 g. (29%) of a product boiling at 54–56° (45 mm.); n_D^{20} 1.4768.

Diethyl Cyclobutylmethyl Alkyl Malonates.—These were prepared by a method previously described,[8] by the condensation of cyclobutylmethyl bromide with diethyl mono-alkyl malonates.

TABLE II

DIETHYL CYCLOBUTYLMETHYL ALKYL MALONATES: $C_4H_7CH_2CH(CO_2H)R$

R =	B. p., °C.	n_D^{25}	d_4^{25}	Calculated, %		Found, %	
				C	H	C	H
n-C_8H_{17}	160–163 (3 mm.)	1.4558	0.9558	70.52	10.67	70.11	10.65
n-C_9H_{19}	168–171 (2.8 mm.)	1.4569	.9552	71.12	10.81	70.82	10.84
n-$C_{10}H_{21}$	177–181 (3 mm.)	1.4578	.9466	71.68	10.95	71.30	10.94
n-$C_{11}H_{23}$	188–191 (3.2 mm.)	1.4582	.9458	72.19	11.08	71.69	11.05
n-$C_{12}H_{25}$	196–199 (3 mm.)	1.4590	.9393	72.66	11.19	72.59	11.23

Cyclobutylmethyl Alkyl Acetic Acids.—These were prepared from the malonic acids by a method previously described.*

TABLE III

CYCLOBUTYLMETHYL ALKYL ACETIC ACIDS: $C_4H_7CH_2CH(CO_2H)R$

R =	B. p., °C.	n_D^{25}	d_4^{25}	Calculated, %		Found, %	
				C	H	C	H
n-C_8H_{17}	150–152 (2 mm.)	1.4615	0.9154	74.94	11.74	74.31	11.78
n-C_9H_{19}	177–181 (3.5 mm.)	1.4622	.9124	75.53	11.90	75.06	11.84
n-$C_{10}H_{21}$	176–179 (2.7 mm.)	1.4628	.9095	76.05	12.02	75.93	11.95
n-$C_{11}H_{23}$	188–192 (2.5 mm.)	1.4635	.9080	76.52	12.14	76.05	12.08
n-$C_{12}H_{25}$	204–205 (2 5 mm.)	1.4642	.9046	76 95	12.26	76.72	12.20

Summary

A series of cyclobutylmethyl alkyl acetic acids has been prepared and tested for bactericidal action to acid-fast bacteria.

URBANA, ILLINOIS

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[8] Adams, Stanley and Stearns, THIS JOURNAL, 50, 1475 (1928).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE KINETICS OF THE THERMAL DISSOCIATION OF PROPANE AND THE BUTANES[1]

BY ROBERT N. PEASE AND ELFORD S. DURGAN

RECEIVED NOVEMBER 29, 1929 PUBLISHED MARCH 6, 1930

Recent work[2] has indicated that the thermal dissociations of the paraffin hydrocarbons (other than methane) are homogeneous first-order reactions yielding as primary products mono-olefins, and a lower paraffin or hydrogen. This work has all been of a more or less exploratory nature, and it has seemed worth while to make a somewhat more thorough study of the behavior of these compounds. Of especial interest are the alternative reactions which take place. These can be conveniently studied for propane and the butanes, since in these cases the reactions are not too numerous, and yet exhibit considerable variety. Consequently, we have carried out an investigation of the dissociation of these compounds, paying special attention to the rates as affected by dilution and by contact with glass surface, and to the relative rates of the simultaneous reactions and their temperature coefficients.

Method.—From the experimental standpoint the chief problem is one of analysis. The exit gas contains (in the case of butane) much of the original hydrocarbon along with nitrogen, hydrogen, methane, ethane, ethylene, propylene and butylene. A complete quantitative separation is a matter of considerable difficulty. What we were interested in was a determination of the fractions of hydrocarbon reacting according to (for butane)

$$C_4H_{10} \longrightarrow C_4H_8 + H_2 \qquad (1)$$

$$C_4H_{10} \longrightarrow C_3H_6 + CH_4 \qquad (2)$$

$$C_4H_{10} \longrightarrow C_2H_4 + C_2H_6 \qquad (3)$$

Assuming that no other reactions enter in, a determination of hydrogen, methane and ethane in comparison with the amount of hydrocarbon taken would give the necessary data. A comparison of the total of these three in the off-gas with the amount of hydrocarbon reacting and the total of olefins formed would give *a* check on the correctness of the assumption that the above reactions are the only ones of importance.

It will be noted that in the case of butane the saturated hydrocarbons

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[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 cooperation of the Central Petroleum Committee of the National Research Council Professor Hugh S Taylor of Princeton University is Director of Project No. 7.

[2] Pease, THIS JOURNAL, **50, 1779 (1928);** Frey and Smith, *Ind. Eng. Chem.,* **20, 948 (1928);** Hurd "Pyrolysis of Carbon Compounds," The Chemical Catalog Company, Inc., New York, **1929,** pp. 46, etc ; Hurd and Spence, THIS JOURNAL, **51,3353** (1929).

in the off-gas divide into the highly volatile methane and ethane, and the relatively non-volatile butane. A separation by fractionation should then be easy, and is found to be so. In the case of propane, only hydrogen, methane and propane are to be determined, and, of course, the gas analysis always permits of expressing total hydrocarbons in terms of two such. We have in both cases resorted to fractionation, and have obtained unequivocal results as to the proportions of saturated hydrocarbons and hydrogen. The proportions of olefins do not stand out so clearly but the relative amounts in different fractions are such as would be expected from the nature of the saturated products.

Our method of fractionation was as follows. The off-gas was collected over mercury in an aspirator bottle. This bottle could be connected to another such through a small trap of 5 cc. capacity. This trap was cooled either to −180° (with liquid air) or to −116° (with solid–liquid ethyl bromide). The first goal was the removal of the bulk of the original hydrocarbon, which always preponderated in the off-gas. This was done by passing the gas slowly through the trap at −116°, and then evaporating one-fourth to one-half of the condensate. The remainder contained no saturated hydrocarbon but the original, along with varying amounts of olefins. The remaining gas (uncondensed plus evaporated) was again passed through the trap at −116°, where a part condensed. Keeping the trap at −116°, the condensate was pumped (using one aspirator bottle as a sort of Töpler pump) until only minimal amounts of gas could be removed. The residue again contained nothing but the original hydrocarbon and olefins Finally, the remaining gas was condensed at −180°, and again pumped. The pumped-off gas consisted only of hydrogen, nitrogen and methane. This left a residue which was warmed to −116°, and pumped for the removal of ethane (and ethylene) and the rest of the methane. The residue from this treatment usually amounted to 1 to 2% of the total gas. It was combined with the residue from the second pumping at −116° on the assumption that it represented the last traces of original hydrocarbon and higher olefins.

By this method, we obtained one fraction containing hydrogen and methane, another containing methane and ethane, and a third containing the original hydrocarbon. Results could then be expressed in terms of these substances and of the total of olefins.

Experiments were carried out by the flow method. The gases passed from tanks through flowmeters to a reaction tube of known volume contained in an electric tube-furnace. The temperature of the latter was taken with a two-junction chromel–alumel thermocouple. The gases had the following analyses

	Percentage						
	C_5H_{12}	C_4H_{10}	C_3H_8	C_2H_6	H_2	N_2	O_2
n-Butane	2 6	94.8	..	...		1.2	1 4
Isobutane	...	98.3	..	...	..	1.2	0.5
Propane	...	..	96 3	3.0	..	0.5	0.2
Hydrogen	...	..	..	...	99 3	0.5	0.2
Nitrogen	...	..	..	...	..	98.5	1.5

Calculation of Velocity Constants,—The first-order velocity constants which appear in the tables were calculated from the ordinary expression

$$k_1 = \frac{2.303}{t} \log_{10} \frac{100}{100 - x}$$

where t is time in seconds and x is percentage conversion. The time was calculated from the volume of the reaction tube and the average of the inflow and outflow rates. The percentage dissociation is the average calculated from the amount of hydrocarbon reacting, the amount of olefins formed and the amount of hydrogen, methane and ethane formed.

Results

Effect of Packing.—If the reactions take place exclusively in the gas phase, an increase in glass surface, brought about by packing the reaction tube with broken glass, should not alter the percentage conversion. Data are presented in Table I in which the reactions in empty and in packed tubes are compared. It will be noted that in general the rate is slightly greater in the packed tube. However, in view of the fact that the packing increases the surface by a factor of about 10, and only increases the rate at most by 10%, we can safely conclude that not more than 1% of the reaction in the empty tube is heterogeneous. The rate increase in the packed tubes may also be due to somewhat better heat transfer in this case, since the reactions are endothermic and would tend to maintain a somewhat lower temperature in the empty tube.

TABLE I

EFFECT OF PACKING THE REACTION TUBE

H.C. and temp.	Reaction tube	Time, sec.	Volumes in cc. at 0° and 1 atm.						Conv., %	k_1
			H.C.		Formed					
			In	Reacted	H_2	CH_4	C_2H_6	C_nH_{2n}		
C_3H_8 at 650°	Empty	12.0	346	69	31	45	..	68	20.5	0.019
	Packed	11.5	345	70	31	41	..	71	20.6	.020
n-C_4H_{10} at 625°	Empty	12.5	341	69	8	48	20	79	22.0	.020
	Packed	12.4	351	78	9	50	21	86	23.7	.022
	Packed[a]	12.4	358	77	8	50	22	85	22.6	.021
Iso-C_4H_{10} at 600°	Empty	25.8	356	62	31	28	4	64	17.7	.0076
	Packed	26.1	354	62	33	31	3	67	18.4	.0078
Iso-C_4H_{10} at 650°	Empty	5.3	315	84	38	43	7	81	26.7	.0059
	Packed	5.1	319	86	35	38	4	74	24.8	.0056

[a] This tube was rinsed with 20% potassium chloride solution, with the view of poisoning any "active spots" on the glass surface.

Effect of Dilution with Nitrogen.—If the reactions are first-order, the rate should be independent of the concentration Consequently, dilution with an inert gas should not affect the first-order rate-constant. If the reactions were in reality second or higher order, dilution should decrease the first-order constant in proportion. Actually, dilution with an equal volume of nitrogen in general increases the constants somewhat. Pertinent data are presented in Table II. An examination of the results indicates that it is probably the dehydrogenation reaction which causes the trouble. There is relatively more hydrogen formed from the diluted gas than from the undiluted gas. It may be that the dehydrogenation reaction is reversible as is known to be the case with ethane.[3] If this is true, better constants could be obtained with greater dilution and smaller conversions. This, however, would involve greater error in the analysis. Another possible explanation is in terms of heat transfer.

In any case, these data on effect of packing and dilution leave no question but that the reactions are essentially first-order homogeneous gas reactions. It should be pointed out that the discrepancies may be in part the result of analytical error, but since they point so consistently in one direction it is probable that they are real.

TABLE II

EFFECT OF DILUTION WITH EQUAL VOLUME OF NITROGEN

H.C. and temp.	Time, sec.	Diluent	Volumes in cc. at 0° and 1 atm. H.C. In	Reacted	Formed H_2	CH_4	C_2H_6	C_nH_{2n}	Conv., %	k_1
C_3H_8 at 625"	25.7	None	368	60	27	39	..	61	16.9	0.0072
	25.9	N_2	187	37	18	23	..	36	20.4	.0088
C_3H_8 at 650°	12.0	None	346	70	31	45	..	69	22.0	.021
	12.1	N_2	188	44	20	28	..	43	23.9	.023
n-C_4H_{10} at 625°	12.5	None	341	69	8	48	20	79	22.0	.020
	12 5	N_2	186	44	7	26	13	47	24.8	.023
Iso-C_3H_{10} at 600°	25 8	None	356	62	32	28	4	64	17.7	.0076
	26.3	N_2	202	33	20	14	4	40	18.3	.0077
Iso-C_4H_{10} at 625°	5.6	None	367	60	26	25	1	54	15.0	.029
	6.3	N_2	187	29	18	14	1	31	16.6	.029
Iso-C_4H_{10} at 650°	3.5	None	362	68	33	33	2	66	18.5	.058
	3 4	N_2	186	37	20	17	2	36	19.9	.065

Effect of Varying Heating Time.—If the dissociations of propane and the butanes were pure first-order homogeneous gas reactions, the first-order rate constant should not change as the percentage conversion is increased by prolonging the heating time. A number of experiments were carried out to determine whether the constant is in fact constant. The results, which are presented in Table III, show that this is not the case. The constants fall rather rapidly as reaction proceeds. This is in line with what had already been found regarding the effects of diluting with nitrogen. In certain cases it appears that the dehydrogenation reaction is most affected, indicating some re-hydrogenation. In fact, when hydrogen was added initially in one experiment on isobutane at 625°, the amount of hydrogen formed was found to be distinctly decreased.

The lack of constancy is so great that no justifiable extrapolation to zero conversion to give a true constant can be made. This is borne out by the fact that no reasonably constant temperature coefficients and heats of activation can be obtained. Experiments at much lower conversions

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[3] Pease and Durgan, THIS JOURNAL, 50,2715 (1928).

TABLE 111

RUNS AT 1 ATMOSPHERE PRESSURE IN EMPTY REACTION TUBES

H.C.	Temp., °C.	Time, sec.	Volumes in cc. at 0° and 1 atm. H.C. In	Reacted	Formed H_2	CH_4	C_2H_6	C_nH_{2n}	Conv., %	k_1
C_3H_8	625	257	368	60	27	39	..	61	16.9	0.0072
	625	53.2	339	92	32	59	..	81	26.0	.0057
C_3H_8	650	5 5	313	43	21	26	..	47	14.7	.029
	650	12.0	346	70	31	45	..	69	20 8	.019
n-C_4H_{10}	600	26.0	368	67	6	46	15	70	18.5	.0079
	600	57.0	329	94	8	62	27	101	29.5	.0061
n-C_4H_{10}	625	12.5	341	69	8	48	20	79	22.0	.020
	625	24.2	330	95	10	68	28	107	31.2	.016
n-C_4H_{10}	650	5.3	317	81	10	52	21	89	265	.058
	650	11.4	308	103	13	71	29	114	35.7	.039
Iso-C_4H_{10}	600	25.8	356	62	32	28	4	64	17.7	.0076
	600	57.7	334	79	40	44	4	86	25 2	.0050
Iso-C_4H_{10}	625	5.6	367	60	26	25	1	54	15.0	.029
	625	11.9	356	91	39	41	4	82	24.2	.023
	625	25.7	305	117	48	62	11	104	37.4	.018
Iso-C_4H_{10}	650	3.5	362	68	33	33	2	66	18 5	.058
	650	5.2	316	90	39	43	6	86	27.9	.063
	650	7.5	323	109	46	52	12	97	32.5	.052
	650	13.8	299	137	55	73	14	115	43 8	.042

are called for, but these must necessarily introduce serious errors in analysis. Nevertheless, further work in this direction should be carried out. Several points deserve additional investigation. There is, for example, a good indication that the proportions of the products do not change with temperature. This would say that the heats of activation for the alternative reactions are the same—a fact which, if true, would be of some theoretical importance as evidencing an activation of the molecule as a whole with the alternative reactions sharing in accordance with certain probability factors which were independent of temperature. There is also an indication that the temperature coefficients for the different hydrocarbons are the same, being about 2.75 per 25° on the average corresponding to a heat of activation of 65,000 cal.

Rate at Low Pressures.—The results of three determinations of rate at a pressure of 2 mm. are of interest. These are compared with results at 1 atm. pressure in Table IV.

TABLE IV

RESULTS AT LOW PRESSURE (TEMP., 625")

Gas	Pressure	Time, sec.	Conv., %	k_1
C_3H_8	2 mm.	41	10	0.0026
	1 atm.	53	26	.0057
n-C_4H_{10}	2 mm.	42	21	.0056
	1 atm.	24	31	.016
Iso-C_4H_{10}	2 mm.	41	16	0043
	1 atm.	26	37	,018

The rate is seen to be distinctly less at these lower pressures, as has been found for other first-order reactions, such as the decomposition of ethyl ether.[4] The rate is, however, definitely not lowered sufficiently to suggest a second-order reaction. These results suggest the desirability of carrying out similar measurements over a wide pressure range between a few millimeters and I atmosphere. We plan to study this aspect of the problem further.

Summary

Further investigation of the thermal dissociations of propane and the butane has confirmed the earlier conclusion that these are fundamentally first-order, homogeneous gas reactions. Due probably to such secondary reactions as re-hydrogenation, the first-order constants fall rather rapidly as reaction proceeds. Dilution with nitrogen has the effect of increasing the rate constants somewhat. At pressures of a few millimeters the constants are distinctly less than at 1 atmosphere, but the difference is not sufficient to indicate a reaction order higher than the first.

The temperature coefficient of rate is about 2.75 per 25°, and the heat of activation is about 65,000 cal. for all three substances, and appears to be of the same order of magnitude for the alternative modes of dissociation.

PRINCETON, NEW JERSEY

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

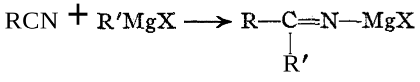
IDENTIFICATION OF NITRILES. PREPARATION OF ALKYL PHENYL KETONES

BY R. L. SHRINER AND T. A. TURNER

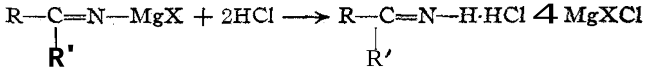
RECEIVED NOVEMBER 29, 1929 PUBLISHED MARCH 6, 1930

Nitriles are usually identified by hydrolyzing them to acids and identifying the latter. When the acid so obtained is aromatic no great difficulty is experienced but in the case of aliphatic acids from alkyl cyanides the isolation and preparation of a solid derivative is more difficult. In an attempt to find an easier means of identifying alkyl cyanides, the reaction with the Grignard reagent was studied.

The following main reactions, involving addition of the Grignard reagent with subsequent decomposition and hydrolysis, were studied by Blaise[1] but no yields were recorded.

(a) 

$$RCN + R'MgX \longrightarrow R{-}\underset{\displaystyle R'}{\underset{|}{C}}{=}N{-}MgX$$

(b) 

$$R{-}\underset{\displaystyle R'}{\underset{|}{C}}{=}N{-}MgX + 2HCl \longrightarrow R{-}\underset{\displaystyle R'}{\underset{|}{C}}{=}N{-}H{\cdot}HCl\ 4\ MgXCl$$

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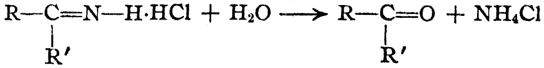
[4] Hinshelwood, *Proc. Roy. Soc. London*, **114A,** 84 (1927).

[1] Blaise, *Compt. rend.,* **132,** **38 (1901).**

(c) 

$$\mathrm{R{-}\underset{\displaystyle R'}{C}{=}N{-}H{\cdot}HCl + H_2O \longrightarrow R{-}\underset{\displaystyle R'}{C}{=}O + NH_4Cl}$$

Baerts[2] obtained four products as the result of the action of ethyl magnesium bromide on propionitrile: diethyl ketone, tri-ethyl carbinol and di- and trimolecular cyano-ethane $(C_2H_5CN)_2$, $(C_2H_5CN)_3$. The yield of ketone was very low.

It was found that by using an excess of the aryl Grignard reagent, phenylmagnesium bromide, the alkyl cyanides could be converted into the corresponding ketones in good yields and the formation of by-products could be avoided. The ketones can be easily converted into solid semicarbazones, hydrazones or oximes and thus identified. This reaction is not only of value for identification but it also furnishes an additional method for the synthesis of the higher alkyl-phenyl ketones. These ketones are usually prepared by the Friedel–Crafts reaction between benzene and the acid chloride or anhydride.[3] However, the alkyl cyanides are much more readily available as starting materials than the higher acid chlorides or anhydrides.

A series of experiments was run with phenylmagnesium bromide and acetonitrile in order to determine the optimum concentrations for the production of the ketone. It was found that a ratio of four moles of the Grignard reagent to one of the nitrile was necessary to give the best results. The use of a larger proportion of phenylmagnesium bromide gave a lower yield of ketone, due probably to conversion of some of the ketone to the carbinol noted by Baerts.[2]

It is not exactly clear why such a large excess of the Grignard reagent is necessary but it seems probable that the excess used converts the nitrile completely to the addition product and hence there is less chance for the polymerization products mentioned by Baerts[2] to form.

Experimental

A typical procedure for carrying out the reaction between phenylmagnesium bromide and a nitrile is as follows.

The phenylmagnesium bromide is prepared in the usual way from 25 g. of magnesium turnings and 160 g. of bromobenzene in 350 cc. of dry ether. A solution of 0.25 mole of the nitrile in 100 cc. of dry ether is run in slowly with stirring during a period of fifteen minutes. The solution is stirred for an hour longer and allowed to stand overnight. The mixture is poured onto 500 g. of ice and 300 cc. of concd. hydrochloric acid. The water layer, which contains the hydrochloride of the ketimide, is separated from the ether layer and refluxed vigorously for one hour. The solution is cooled and extracted with four 200-cc. portions of ether. The ether extract is dried over anhydrous calcium chloride and the ether distilled from a water-bath. The residue is transferred to a small modified Claisen flask and vacuum distilled. The ketones and their properties are recorded in Table I.

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[2] Baerts, Bull. *soc. chim.* belg., 31, 184 (1922).

[3] Noller and Adams, THIS JOURNAL, 46, 1889 (1924).

Preparation of **Semicarbazones.**—One cubic centimeter of the ketone was dissolved in 10 cc. of ethyl alcohol in a test-tube. Water was added until the solution was faintly turbid and the turbidity then removed with a few drops of alcohol. Then 1.0 g. of semicarbazide hydrochloride and 1.50 g. of sodium acetate were added. The solution was vigorously shaken and the test-tube placed in a beaker of boiling water. The water-bath was allowed to cool and at the end of thirty minutes the test-tube was cooled in cold water and scratched with a glass rod. The semicarbazone crystallized out and was filtered. One recrystallization from 50% alcohol gave pure white crystals. Further recrystallization did not change the melting point. They were analyzed for nitrogen by the Kjeldahl method. The properties and analyses are given in Table II.

TABLE I

KETONES OBTAINED BY THE ACTION OF ONE MOLE OF PHENYLMAGNESIUM BROMIDE ON NITRILES

Nitrile	Used (0.25 mole), g.	Ketone	Yield, g.	Yield, %	Properties of ketones B. p., °C. (corr.)	at mm.	d^{20}_{20}	n^{20}_{D}
CH_3CN	10.2	$C_6H_5COCH_3$	21	70	202–205	760	1.020	1.541
C_2H_5CN	13.7	$C_6H_5COC_2H_5$	31	91	115–120	21	1.015	1.534
n-C_3H_7CN	17.2	$C_6H_5COC_3H_7$-n	28.5	77	125–130	21	0.989	1.524
n-C_4H_9CN	20.8	$C_6H_5COC_4H_9$-n	32	79	135–140	25	.988	1.532
n-$C_5H_{11}CN$	24.3	$C_6H_5COC_5H_{11}$-n	36.5	83	145–150	19	.981	1.538
Iso-$C_5H_{11}CN$	24.3	$C_6H_5COC_5H_{11}$-*iso*	22	50	143–148	20	.971	1.533

TABLE II

SEMICARBAZONES FROM PHENYL ALKYL KETONES

Ketone	M. p. (corr.) of semicarbazone, °C.	Nitrogen analysis of semicarbazones, % Calcd.	Found
$C_6H_5COCH_3$	198–199[a]	24.02	[a]
$C_6H_5COC_2H_5$	173–174[b]	21.99	21.75
$C_6H_5COC_3H_7$-n	184–184.5[c]	20.49	20.61
$C_6H_5COC_4H_9$-n	157–157.5	19.65	19.67
$C_6H_5COC_5H_{11}$-n	127–128	18.02	18.32
$C_6H_5COC_5H_{11}$-*iso*	145–146	18.02	18.37

[a] Melting points previously given, 162°, Clarke "Handbook of Organic Analysis," Arnold and Co., 1928; Stobbe [Ann., 308, 123 (1899)] gives 195–198°; Borsche [*Ber.*, 34,4301 (1901)] gives 198–199°.

[b] Blaise, Compt. *rend.*, 133, 1218 (1901), gives 182°; Stobbe and Niedenzuin, *Ann.*, 321, 103 (1902), give 173–175°.

[c] Sorge, *Ber.*, 35, 1074 (1902), gives 188°.

Summary

Phenyl alkyl ketones can be obtained in 50 to 90% yields by hydrolysis of the product formed by the action of phenylmagnesium bromide on alkyl cyanides.

The properties of the ketones and their semicarbazones are described.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE HYGIENIC LABORATORY, U. S. PUBLIC HEALTH SERVICE]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XXIV. THE TWO CRYSTALLINE LACTONES OF *l*-RHAMNONIC ACID[1,2]

BY ERNEST L. JACKSON AND C. S. HUDSON

RECEIVED DECEMBER 2, 1929 PUBLISHED MARCH 6, 1930

Recently we undertook the preparation of *l*-rhamnonic amide in order to determine its exact rotation. Chernoff[3] showed that the amide is dextrorotatory in agreement with the amide rule of rotation[3,4] but the magnitude was not reported. Starting with pure *l*-rhamnose it was planned to prepare crystalline rhamnonic lactone, which has been described by several investigators[5] (m. p. 150–151° and $[\alpha]_D$ $-39°$), and to convert this lactone to the amide. The beautifully crystalline lactone which we obtained readily in good yield proved to be a different substance, however, as it melted much higher (172–181°) and showed an initial $[\alpha]_D$ $-98°$, which decreased fairly rapidly during the first day and then very slowly decreased to $-30°$ at the end of eleven weeks, the temperature being 25–30°. The aqueous solution of the substance was neutral to litmus immediately after preparation at room temperature but it developed an acid reaction after about one minute. Its titration corresponded to the value calculated for rhamnonic lactone. The crystals are evidently a second lactone of *l*-rhamnonic acid, the first lactone being the one for which Schnelle and Tollens[5] gave the earliest accurate description.

A thorough study of the two lactones, especially of the conditions of preparation which favor the formation of each, was undertaken. It led to a most unexpected result. The second lactone, which we at first believed to be a new substance, was unquestionably in the hands of Will and Peters forty years ago, because their accurate crystallographic measurements of the crystals of their *l*-rhamnonic lactone apply closely to our crystals of the second lactone but do not agree at all with measurements, now made for the first time, of crystals of the first lactone.[6] Will and Peters, in an article previous to the one in which they record the crystal measurements, state that their lactone melts at 148°. From this statement it seems evident at the present time that they must have had both

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[1] Publication authorized by the Surgeon General of the U. S. Public Health Service.

[2] No. XXIII was published in THIS JOURNAL, 51, 3631 (1929).

[3] Hudson, *ibid.*, 40, 813 (1918).

[4] Hudson, *ibid.*, **39**, 465 (1917).

[5] Will and Peters, *Ber.*, **21**, 1813 (1888); 22, 1704 (1889); Rayman, *ibid.*, **21**, 2046 (1888); Schnelle and Tollens, *Ann.*, 271, 71 (1892); Fischer and Herborn, *Ber.*, **29**, 1962 (1896).

[6] The crystallographic measurements were made by F. E. Wright and are reported by him in the paper immediately following this.

crystalline lactones under observation and, regarding them as a single substance, measured the melting point of one sample (which happened to be the first lactone) and the crystal angles of a different sample (which happened to be the second lactone). During the progress of our investigation of these lactones, the recent article of VotoEek and BeneS[7] came to our attention and it was recognized at once that the supposedly new *l*-rhamnonic lactone which they have prepared by the reduction of *l*-rhamno-ketonic acid with sodium amalgam is the same substance that we have met with, namely, the lactone which Will and Peters measured crystallographically, the second lactone. Votoček and Beneš have shown that Kiliani[8] recently had this lactone in hand, through the same method of preparation from *l*-rhamno-ketonic acid, though he did not recognize it as belonging in the rhamnose series but considered it to be a lactone of gulomethylonic acid. Since our study approached the subject in a different way from that undertaken by VotoEek and Beneš, who have stated that they are continuing the investigation of the lactones, we decided to complete those phases of our work which concern the rotations, structures and interconversions of these lactones and the preparation of rhamnonic amide from each of them.

The first lactone ($[\alpha]_D$ −39.7°) undergoes only slight change in aqueous solution in the course of several weeks at 25–30°, its specific rotation decreasing to —38.4' in six weeks. From this fact it seems reasonably certain, following the views of Nef,[9] that the first lactone is of the 1,4-ring type. The second lactone ($[\alpha]_D$ −98°) exhibits a much larger and more rapid mutarotation than does the first and is the lactone to which rhamnonic acid initially changes when liberated from solutions of its salts. These facts lead us to assign provisionally the 1,5-ring structure to the second lactone, following the views of Levene and Simms.[10] The evidence for the 1,5-ring structure would be strengthened if the possibility of a 1,3-ring structure for these rapidly mutarotating lactones of the sugar group could be excluded, but in our opinion this cannot now be done.

There is a striking relationship between the rotations of the two *l*-rhamnonic lactones and those of the two d-mannonic lactones which Nef[9] prepared with much care in 1914. The d-mannonic lactone of $[\alpha]_D$ +52° is the one of greater stability, to which the 1,4-ring structure is commonly assigned, and the d-mannonic lactone of $[\alpha]_D$ +111° presumably possesses the 1,5-ring. Writing the configurations in the d-series and reversing therefore the signs of our measurements, which pertain to the *l*-rhamnose series, it is seen that there is a close parallelism here between the *d*-mannose

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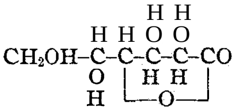
[7] VotoEek and Beneš, *Bull. soc. chim.*, [4] **43**, 1328 (1928).

[8] **Kiliani,** *Ber.*, **55**, 2822 (1922).

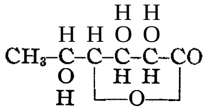
[9] **Nef,** *Ann.*, **403**, 308 (1914).

[10] Levene and Simms, *J. Biol. Chem.*, **65**, 31 (1925).

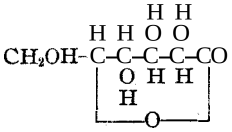
and *d*-rhamnose derivatives. The change of structure of the terminal group from CH_2OH to CH_3 (this carbon atom being symmetric and without rotation) decreases the specific rotation by about 12–13' whether the ring is 1,4 or 1,5.



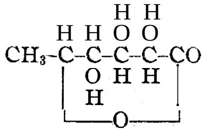
d-Mannonic (1,4)-lactone, $[\alpha]_D$ +52°



d-Rhamnonic (1,4)-lactone, $[\alpha]_D$ +40°



d-Mannonic (1,5)-lactone, $[\alpha]_D$ +111°



d-Rhamnonic (1,5)-lactone, $[\alpha]_D$ +98°

In our initial preparation, which yielded the second 1-rhamnonic lactone, rhamnose was oxidized by bromine water containing barium benzoate as a buffer to prevent the occurrence of strong mineral acidity during the oxidation.[11] Under these conditions rhamnonic acid forms its labile 1,5-lactone. If the buffer is omitted, the free hydrobromic acid which is produced during the oxidation of the sugar catalyzes the change to the stable 1,4-lactone. It has proved possible in these ways to prepare from rhamnose either crystalline lactone at will, or a mixture of them which is readily separated into its constituents by crystallization from hot acetone, in which the first lactone is much more soluble. Starting, with 'crystals of the first or stable 1,4-lactone, the second may be produced by forming in solution a salt of rhamnonic acid (e. g., lead rhamnonate), decomposing this in the cold by an appropriate precipitant of the metal (*e.* g., hydrogen sulfide) and concentrating the aqueous solution under diminished pressure to crystallization. Starting with crystals of the second or labile 1,5-lactone, dissolving them in dilute hydrochloric acid and evaporating the solution to dryness on the steam-bath yields a crystalline residue which consists almost entirely of the first lactone. Omitting the hydrochloric acid, this change takes place partially when an aqueous solution of the second lactone is evaporated on the steam-bath. These methods of preparation illustrate again the close analogy between the lactones of the rhamnose and mannose series, because the methods are indeed those which Nef[9] devised for the interconversion of the two mannonic lactones.

The reaction of ammonia with either the first or the second I-rhamnonic lactone dissolved in absolute alcohol yields I-rhamnonic amide. This result confirms the view that we are dealing with two isomeric lactones of *l*-rhamnonic acid. The rotation of the amide in water was found to be

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[11] Hudson and Isbell, This Journal, 51,2225 (1929).

$[\alpha]_D^{20}$ +27.7°, which agrees with the amide rule of rotation. Its melting point is 134–134.5°.

Experimental Part

Oxidation of Rhamnose with Bromine Water in the Presence of Barium Benzoate.—Eight cc. of bromine was added to an ice cold solution of 24.4 g. of pure rhamnose monohydrate and 80 g. of barium benzoate in 1 liter of distilled water. The bromine dissolved on shaking during fifteen minutes and the solution was kept in the dark at room temperature for about forty hours, It then gave only a slight reduction of Fehling's solution. The excess bromine was removed with a stream of air, the benzoic acid was filtered off and the barium was precipitated quantitatively with 5 *N* sulfuric acid (about 82 cc.). After the addition of 10 g. of decolorizing carbon, the barium sulfate was filtered off by suction. The hydrobromic acid was neutralized with silver carbonate (54 g.), the silver bromide was filtered off and excess silver was removed as sulfide. The solution was left overnight in the refrigerator and then distilled under diminished pressure to about 250 cc. (bath temperature 75–80°). It was extracted with chloroform to remove benzoic acid and distilled under reduced pressure until crystallization began (40–50 cc.). After the solution had stood overnight in an evacuated desiccator over calcium chloride, the crystals, consisting entirely of the second rhamnonic lactone, were filtered off and washed with a little acetone. The mother liquor was concentrated under reduced pressure to about 10 cc. (bath temperature 45–50°) and evaporated to dryness in a vacuum desiccator. The residue was a mixture of the two rhamnonic lactones containing 0.2 g. of material insoluble in hot acetone, probably a salt. The lactones were separated by a fractional crystallization from acetone. The yield of the second lactone was 11.9 g. or 55% of the theoretical and of the first lactone was 4.8 g. or 22%. The second lactone melts at 172–181°. The melting point varies somewhat with the manner of heating and is not a sharp criterion of purity.

Anal. Calcd. for $C_6H_{10}O_5$: C, 44.43; H, 6.22. Found: C, 44.25; H, 6.11.

In aqueous solution the second lactone remains neutral to litmus for about one minute. Its titration with sodium hydroxide solution corresponds to rhamnonic lactone: 0.3914 g. of substance required 24.66 cc. of 0.1 N sodium hydroxide, the calculated amount being 24.14 cc. It shows $[\alpha]_D^{23}$ −98.4° seven minutes after solution (0.7910 g. of substance, 25 cc. of solution in water, 2-dcm. tube; rotation, 6.23° to the left). The rotation gradually falls and after six hours at room temperature $[\alpha]_D^{24}$ is −61.0°. At the end of eleven weeks $[\alpha]_D^{28}$ is −30.1°. When a solution of the second lactone in water had stood for about seven weeks it was distilled under reduced pressure to dryness and the residue (1.8 g.) was recrystallized from acetone. This gave 1.1 g. of the first lactone and only 0.5 g. of the second lactone, showing that the more stable first lactone had formed in solution at the expense of the unstable second lactone.

The first lactone melts at 148–150° and shows $[\alpha]_D^{23}$ −39.7° eight minutes after solution (0.9856 g. of substance, 25 cc. of solution in water, 2-dcm. tube; rotation, 3.13° to the left). After seventy-five hours $[\alpha]_D^{21}$ was −38.9° and at the end of six weeks $[\alpha]_D^{23}$ was −38.4'.

The first lactone is much more soluble in acetone than the second. The solubilities were determined at 1.0 ± 0.5°. Five cc. of anhydrous acetone was found to dissolve 0.0677 g. of the first lactone from undersaturation and 0.0693 g. from supersaturation, which gives 1.37 g. as the average value for 100 cc. of acetone. Ten cc. of anhydrous acetone dissolved 0.0142 g. of the second lactone from undersaturation and 0.0157 g. from supersaturation, the mean value for 100 cc. of acetone being 0.1495 g.

The two lactones do not appear to form mixed crystals from acetone. Crystals Characteristic of each pure substance separated side by side during their fractional crystallization. On one occasion these were separated mechanically as well as possible. One portion melted at 166–172° and showed $[\alpha]_D^{24}$ $-94.7°$, while the other melted at 145–147° and gave $[\alpha]_D^{24}$ $-43.4°$.

In preparing the second lactone directly from rhamnose by oxidation with bromine water in the presence of a buffering salt, it is necessary to avoid conditions of high mineral acidity acting for a prolonged time during the various separations, because the change to the first lactone is catalyzed by strong acids. For example, a preparation was carried out by the indicated directions except that the solution was kept at room temperature for about forty hours after the quantitative precipitation of the barium with sulfuric acid and before the removal of the hydrobromic acid with silver carbonate; the resulting lactone was the first or stable one, obviously because the free hydrobromic acid had catalyzed its production from the labile or second lactone during the forty hours of standing.

The oxidation of rhamnose by bromine water in the absence of a buffering salt is a slow process and the resulting lactone is principally the first form, though a small amount of the second lactone is also obtained. In one experiment the directions of Fischer and Herborn[5] were accurately followed; from 6 g. of pure rhamnose monohydrate and 12 g. of bromine in 36 cc. of water, after standing for three days at room temperature, a yield of 57% of first lactone (m. p. 146–149°) and 6% of second lactone (m. p. 168–173°) was obtained. The lactones were separated by the use of acetone. This experiment explains how Will and Peters could have had both lactones in hand, since they oxidized rhamnose under similar conditions; it seems probable that the other earlier investigators also crystallized both lactones in the mixed state. Indeed, when the crystals of the two lactones are once recognized by the eye it seems remarkable that the separate identity of the second form has been so long overlooked.

Conversion of the Second Rhamnonic **Lactone** to the First.—One g. of pure second lactone was dissolved in 15 cc. of distilled water to which was added 0.3 cc. of concentrated hydrochloric acid. The solution was evaporated to dryness on the water-bath and the solid crystalline residue was heated with occasional stirring until a test with litmus paper showed no volatile acidity. The substance was thrice washed with ether to remove possible traces of hydrogen chloride. The product was almost colorless; m. p., 149–151°. It showed $[\alpha]_D^{23}$ $-40.1°$. After one recrystallization from acetone it melted at 147–148° and gave $[\alpha]_D^{22.5}$ $-39.0°$, values which indicate a complete conversion of the second lactone to the first. These directions are those which Nef[9] devised for converting the second mannonic lactone into the first and it is seen that they apply excellently to the similar transformation in the rhamnose series.

Conversion of the **First** Rhamnonic **Lactone** to the Second.—A solution of 2 g. of pure first lactone in 50 cc. of distilled water in which was suspended 5 g. of pure basic lead carbonate was boiled under a reflux condenser for two hours. After filtering off excess lead carbonate the lead rhamnonate was decomposed by passing hydrogen sulfide through the ice cold solution. The filtered solution was distilled immediately under reduced pressure to a thin sirup, the bath temperature at the end being 40–45°. On evaporating the sirup to dryness in a vacuum desiccator, 1.9 g. of solid resulted. After recrystallization from acetone the yield of second lactone was 1.8 g.; m. p. 168–173°. Again, these directions are the same in principle as those which Nef[9] devised for converting the first mannonic lactone into the second; where he decomposed a calcium salt with oxalic acid we preferred to use a lead salt and hydrogen sulfide.

Preparation of *l*-**Rhamnonic Amide** from the First and from the Second Rhamnonic Lactone.—To 150 cc. of absolute ethyl alcohol, saturated with dry ammonia gas, 4.7 g. of the second lactone melting at 167–173° was added. The lactone dissolved on shaking and the rhamnonic amide which crystallized from the solution was filtered off and the filtrate concentrated under reduced pressure to a small volume. The crystals thus obtained were filtered off and the filtrate evaporated to dryness in an evacuated desiccator. The yield of crude rhamnonic amide was theoretical. It was recrystallized to constant rotation from absolute alcohol, from which it crystallized as colorless plates. After drying in an evacuated desiccator over calcium chloride it melted at 126–129°. On drying to constant weight in a vacuum at **76°** in the presence of phosphorus pentoxide, it lost **4.51%** in weight and then melted at 134–134.5° and gave $[\alpha]^{20}_{D}$ +27.7° (0.6043 g. of substance, **25** cc. of solution in water, 2-dcm. tube; rotation, 1.34° to the right).

Anal. Calcd. for $C_6H_{13}O_6N$: C, 40.20; H, **7.31**; N, 7.82. Found: C, 40.02; **H, 7.29**; N (Kjeldahl), 7.89.

The repetition of this preparation, using **4** g. of the first lactone, gave a theoretical yield of the same *l*-rhamnonic amide of m. p. 134–134.5° and $[\alpha]^{25\ 5}_{D}$ +27.6°. **A** mixed melting point of the amides from the two lactones showed no depression. The amide is soluble in water, nearly insoluble in cold absolute alcohol or ether and soluble in hot absolute alcohol.

Summary

The oxidation of *l*-rhamnose with bromine water containing barium benzoate as a buffer yields a second crystalline lactone of l-rhamnonic acid, of m. p. 172–181° and $[\alpha]_D$ −98° in aqueous solution. It mutarotates rapidly and therefore probably possesses the 1,5-ring. The well-known first rhamnonic lactone, of m. p. 148–150° and $[\alpha]_D$ −40°, is of the stable type showing very slow mutarotation and it therefore probably possesses the 1,4-ring. Methods for producing either lactone at will from the oxidation of rhamnose with bromine water are shown and Nef's methods for converting each of the two lactones of mannonic acid into the other are found to be applicable to the rhamnonic lactones. A comparison of the rotations of the two rhamnonic lactones with the two mannonic lactones shows an interesting relation between structure and rotation. Pure l-rhamnonic amide, of m. p. 134–134.5° and $[\alpha]^{20}_{D}$ +27.7°, is described. Its sign of rotation agrees with the amide rule.

WASHINGTON, D. C.

RHAMNONIC LACTONE 1,4 AND 1,5. CRYSTALLOGRAPHICAL AND OPTICAL PROPERTIES

By F. E. Wright

Received December 2, 1929 Published March 6, 1930

The crystals of the two rhamnonic lactones, whose crystallographic and optical properties are described in this paper, were prepared by Drs. Ernest L. Jackson and C. S. Hudson[1] from a solution in acetone. The 1,5-crystals are smaller than the 1,4-crystals and are more perfectly developed. The 1,5-crystals proved to be the crystals described by Will and Peters[2] in their work on rhamnonic lactone.

Rhamnonic Lactone 1,5.—Crystallized from solution in acetone. Crystal system, orthorhombic, class bisphenoidal; axial ratio, $a:b:c$ = 0.6874:1:1.2592. Two different lots of crystals were available for measurement.

Crystals of the first lot are in the form of short, stocky prisms 1 to 3 mm. long and 0.5 to 1 mm. thick. They are bounded by the forms (110), (010) and (101) chiefly; the forms (100), (012), (001), (111) occur as smaller facets; form (021) is rare and was observed only on a single crystal; the basal pinacoid is never well developed. The crystals are commonly grouped together in clusters and radiate from a common center; six or eight crystals may be so arranged. Some of the crystals are doubly terminated; but most of the crystals are attached at one end to a cluster and exhibit crystal faces only at the free end. On some of the crystals the end faces are symmetrically developed; but a number show a tendency toward unequal growth of the dome faces 101 and $\bar{1}01$, also 011 and $0\bar{1}1$. The forms (110) and (101) on many crystals exhibit small, beautiful etch figures that emphasize the sphenoidal hemihedrism of the crystals. The etch figures on 101 are three-sided with curved boundaries (Fig. 1) and with one of the sides parallel with the edge between 101 and $1\bar{1}0$; similarly the etch figures on 110 are three-sided with curved boundaries and with one side parallel with the edge between 110 and 101. Etch figures were not observed on the prism face $1\bar{1}0$.

In the second lot of crystals the form is more nearly equant, and the tendency to form clusters is less pronounced. The crystals are doubly terminated and range from 1 to 2 mm. in length and somewhat less in thickness. They are bounded by the forms (110), (010), (101), (011) and (012) chiefly; the pyramid (111) appears as small triangular facets; the forms (010) and (001) are less prominent with (001) poorly developed or failing altogether. No face is etched. The shape of the crystals is shown in Fig. 2.

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[1] Their article immediately precedes the present paper.

[2] Will and Peters, *Ber.*, 22, 1704 (1889).

The fracture is conchoidal; no cleavage was observed.

Six carefully selected 1,5-crystals were measured on a Goldschmidt two-circle goniometer with reducing attachment. Many of the observed reflection signals were single and excellent; many were multiple and poor. The average of 8 best unit prism angles thus obtained is 69°00′ with departures of ±1′ from the mean. The average polar distance ρ for the form (101) is 61°22′, the values measured on 10 faces ranging from 61°13′ to 61°31′. For (011) the mean polar distance is 51°33′ for 7 faces, the observed angles ranging from 51°22′ to 51°40′. The axial ratios were computed by the systematic two-circle method for all satisfactory faces. On the basis of the values thus obtained the table of angles for this form is as follows.

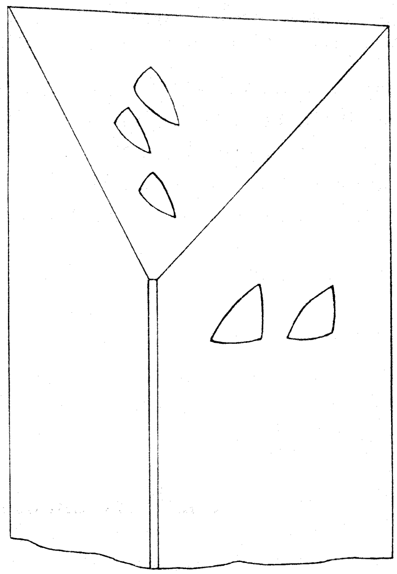

Fig. 1.—Etch figures observed on the forms (110) and (101) of rhamnonic lactone-1,5.

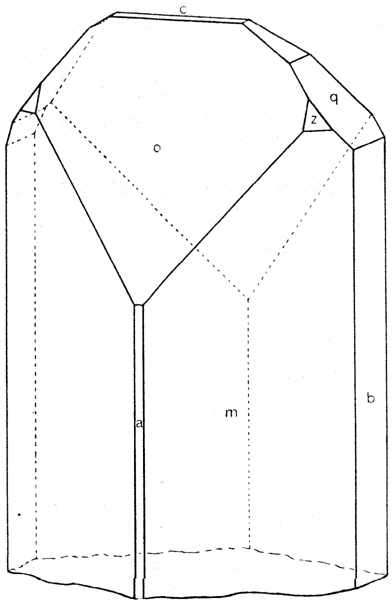

Fig. 2.—Crystal of rhamnonic lactone-1,5.

Crystals of the 1,5-substances were also obtained from a solution in alcohol. These crystals are in the form of needles and clusters of needles of subparallel arrangement. The prism faces on some of the crystals are sufficiently developed to permit measurement on the goniometer; their interfacial angle is 69°00′, characteristic of the form (110). The terminal facets are invariably rounded and yield no reflection signals. Many of the needles taper at the end and show no terminal faces.

Under the microscope and between crossed nicols all 1,5-crystals extinguish parallel with the elongation. Birefringence is strong. Sections

TABLE I

RHAMNONIC LACTONE 1,5

$a = 0.6874$ $a_0 = 0.5459$ $p_0 = 1.8319$
$c = 1.2592$ $b_0 = 0.7942$ $q_0 = 1.2592$

No.	Letter	*Symb.* Crdt.	Miller	φ	ρ	ξ_0	η_0	ξ	η	x Prisms $x:y$	y	d $\tan\rho$
1	c	0	001	....	0°00′	0°00′	0°00′	0°00′	0°00′	0	0	0
2	b	0 ∞	010	0°00′	90 00	0 00	90 00	0 00	90 00	0	∞	∞
3	a	∞ 0	100	90 00	90 00	90 00	0 00	90 00	0 00	∞	0	∞
4	m	∞	110	55 30	90 00	90 00	90 00	55 30	34 30	1 4548	∞	∞
5	n	∞ 2	120	36 02	90 00	90 00	90 00	36 02	53 58	0.7274	∞	∞
6	k	0 $^1/_2$	012	0 00	32 12	0 00	32 12	0 00	32 12	0	0.6296	0 6296
7	q	01	011	0 00	51 33	0 00	51 33	0 00	51 33	0	1.2592	1 2592
8	r	02	021	0 00	68 20	0 00	68 20	0 00	68 20	0	2.5184	2 5184
9	o	10	101	90 00	61 22	61 22	0 00	61 22	0 00	1.8319	0	1 8319
10	z	1	111	55 30	65 47	61 22	51 33	48 44	31 06	1.8319	1.2592	2 2229

parallel with the prism face exhibit in convergent polarized light an optic axis emerging at an angle of about 11° with the normal to the plate. The plane of the optic axes is normal to the elongation and parallel with the basal pinacoid (001). The refractive indices were measured by the immersion method under the microscope. The values are listed for sodium light and may be in error by ±0.002.

$$\alpha = 1.514 \quad \beta = 1.546 \quad \gamma = 1.592$$

Optical orientation

$$a = \gamma \quad b = \alpha \quad c = \beta$$

The optic axial angle of a crystal immersed in a liquid of refractive index β was measured directly on an axial angle apparatus and found to be

$$2V_\gamma = 82°10' \text{ for red light } (0.65\mu)$$
$$2V_\gamma = 82°12' \text{ for blue light } (0.48\mu)$$

Dispersion of optic axes slight. Optical character positive.

The foregoing crystallographical and optical data agree very closely with the few data listed by Will and Peters in their original paper. The axial ratios are

$a:b:c = 0.6873:1:1.2600$ **Will and Peters**
$a:b:c = 0.6874:1:1.2592$ **Wright**

Observed forms

(110) (011) (012) (001) **Will and** ***Peters***
(110) (011) *(012)* (001) (010) (100) *(120) (021) (111) (101)* **Wright**

No cleavage observed.

Plane of optic axes is (001).

On a prism face (110) observed in convergent polarized light an optic axis emerges at an angle of 30° (Will and Peters) or 10° (Wright) with the normal to the plate and in the direction of the b axis.

In view of this agreement there is no question that rhamnonic lactone 1,5 is the substance measured crystallographically and optically by Will and Peters.

Rhamnonic **Lactone 1,4.**—Crystallized from solution in acetone. Crystal system orthorhombic; axial ratio $a:b:c = 0.7772:1:0.3484$. The crystals are prismatic in shape and measure up to 15 mm. in length and 4 mm. in width. In general they are not so clear and well developed as the 1,s-crystals. Only one doubly terminated crystal was observed. In comparison with the wedge-like terminations of the 1,5-crystals, the 1,4-crystals are bluntly terminated by the forms (011), (101) and (111). The prism (120) dominates the prism zone with (110) and (010) subordinate in character; the form (120) might have been chosen as unit prism; but by so doing the dome and pyramid faces would have had larger indices and this would not be advantageous. The shape of the crystals is illustrated in Figs. **3** and 4.

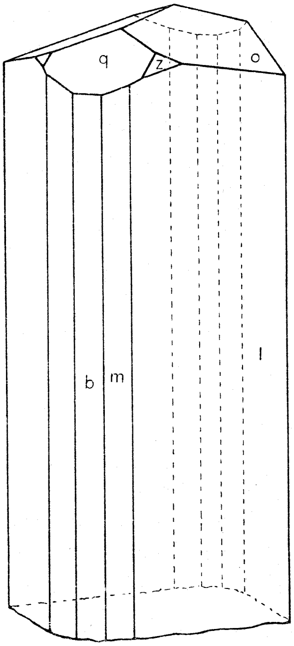

Fig. 3.—Crystal of rhamnonic lactone-1,4.

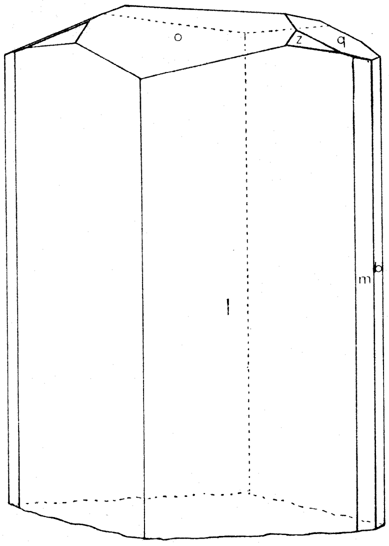

Fig. 4.—Crystal of rhamnonic lactone-1,4 showing the b axis pointing toward the observer. Crystal turned at 90° to the position shown in Fig. **3.**

In Fig. 4 the crystal is shown turned at 90° to its position in Fig. **3,** and gives its appearance had the prism (120) been selected as unit prism.

The crystals occur in irregular clusters and groups. Etch figures were not observed. Many of the crystal faces are poorly developed and irregular and show crystal growth phenomena; these are not favorable to the production of clear-cut etch figures. No cleavage was observed; the fracture is conchoidal.

Five small crystals of the 1,4-substance were measured on the goniometer. The faces on the larger crystals gave multiple signals and were useless for goniometric work. In the prism zone the angle between the faces $120:\bar{1}20$

averages 65°30′; angle $110:1\bar{1}0 = 75°42′$ (mean of 11 interfacial angles); the average polar distance for (011) is 19°13′ (mean of 10 values ranging from 19°09′ to 19'20') for (101) the polar angle p = 24°09′ (average of 7 values ranging from 24'00' to 24°13′). The unit pyramid faces are small and on no single crystal were more than two faces of the complete form observed. In the development of the crystal faces there is a noticeable lack of symmetry; this may indicate a class other than the holohedral class of the orthorhombic system.

In Table II are listed the angles and data for the several observed forms as computed from the axial ratios deduced by the usual methods from the averages of the best measured angles.

TABLE II

RHAMNONIC LACTONE 1,4

$a = 0.7772$ $a_0 = 2.2308$ $p_0 = 0.4483$
$c = 0.3484$ $b_0 = 2\ 8703$ $q_0 = 0.3484$

No.	Letter	Symb.	Miller	φ	ρ	ξ_0	η_0	ξ	η	x Prisms $x{:}y$	y	d
1	b	0 ∞	010	0°00'	90°00′	0°00′	90°00′	0°00′	90°00′	0	∞	m
2	m	∞	110	52 09	90 00	90 00	90 00	52 09	37 51	1.2867	∞	∞
3	1	∞ 2	120	32 45	90 00	90 00	90 00	32 45	57 15	0.6434	∞	∞
4	o	01	011	0 00	19 13	0 00	19 13	0 00	19 13	0	0.3484	0.3484
5	q	10	101	90 00	24 09	90 00	24 09	90 00	24 09	0 4483	0	0.4483
6	z	1	111	52 09	29 35	24 09	19 13	22 57	17 38	0.4483	0.3484	0.5678

The refractive indices were measured by the immersion method. The values are given for sodium light and may be in error ±0.002. The principal refractive indices are

$$\alpha = 1.497 \quad \beta = 1.525 \quad y = 1.532$$

Optical orientation

$$a = y \quad b = \beta \quad c = \alpha$$

The plane of the optic axes is parallel with the elongation of the crystal. Optical character negative; optic axial angle small. The optic axial angle was measured directly both under the microscope and on an axial angle apparatus:

$2Ea = 80°44′$ for *red* light (0 65μ)
$2E_\alpha = 76°30′$ for *blue* light *(0.48μ)*

The dispersion of the optic axes is large and much greater than in the 1,5-crystals, in which it is hardly perceptible. Extinction is parallel and negative. Plane of the optic axes is the brachy-pinacoid (010).

These crystallographical and optical data prove conclusively that rhamnonic lactone 1,4 is quite different from rhamnonic lactone 1,5. The two substances are most easily distinguished under the microscope. All of the optical constants are so different that even in very fine grains the determination should be easy.

Summary

The crystallographical and optical properties of the 1,4- and 1,5-lactones of rhamnonic acid have been measured. The results show conclusively

that the *l*-rhamnonic lactone which Will and Peters measured in 1889 was the 1,5- rather than the 1,4-lactone.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS]

PREPARATION AND BACTERIOLOGICAL ACTION TOWARD B. LEPRAE OF CERTAIN OLEFINIC ACIDS. XVII[1]

BY E. BROWNING, H. W. WOODROW AND ROGER ADAMS

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Although the various cyclopentenyl alkyl acetic acids showed only slightly greater bactericidal action to B. *Leprae* than the corresponding cyclopentyl acids, a more careful study of the effects of an olefin linkage substituted in various dialkyl acetic acids has been undertaken. Representatives of three types of acids were prepared, allyl alkyl acetic acids, undecenyl alkyl acetic acids, and certain dialkyl acetic acids with the olefin linkage in the α,β-position. The bacteriological results are shown in Table I. The authors are indebted to Dr. W. M. Stanley for making these tests.

TABLE I

BACTERIOLOGICAL ACTION TOWARD *B. Leprae*

	Dilutions of sodium salts in thousands												
	5	15	25	50	62	74	85	100	125	155	192	250	330
	Allyl alkyl acetic acids												
$C_3H_5CH(CO_2H)C_9H_{19}$-*n*	−	−	−	−	−	−	+	+	+	+	+	+	+
$C_3H_5CH(CO_2H)C_{10}H_{21}$-*n*	−	−	−	−	−	−	−	±	+	+	+	+	+
$C_3H_5CH(CO_2H)C_{11}H_{23}$-*n*	−	−	−	−	−	−	−	−	−	+	±	+	+
$C_3H_5CH(CO_2H)C_{12}H_{25}$-*n*	−	−	−	−	−	−	−	−	−	*	−	−	+
$C_3H_5CH(CO_2H)C_{13}H_{27}$-*n*	−	−	−	−	−	−	−	−	−		+	+	+
$C_3H_5CH(CO_2H)C_{14}H_{29}$-*n*	−	−	−	−	−	−	−	−	+	+ +	+	- I	-
	Undecenyl alkyl acetic acids												
$C_{11}H_{21}CH(CO_2H)C_4H_9$-*n*	−	−	−	−	−	−	−	−	−	−	−	+	+
$C_{11}H_{21}CH(CO_2H)C_5H_{11}$-*n*	−	−	−	−	−	−	±	±	±	−	*	*	+
$C_{11}H_{21}CH(CO_2H)C_6H_{13}$-*n*	−	−	−	−	±	±	*	+	+	+	±	+	+
$C_{11}H_{21}CH(CO_2H)C_7H_{15}$-*n*	−	−	−	±	+	±	±	+	+	+	+	+	+
	α,β-Unsaturated acids												
$C_3H_7CH{=}C(CO_2H)C_4H_9$-*n*	−	+	+	+	+	+	+	+	+	+	+	+	+
$C_6H_{13}CH{=}C(CO_2H)C_7H_{15}$-*n*	−	−	−	−	−	−	−	−	−	−	−	±	+
$C_7H_{15}CH{=}C(CO_2H)C_8H_{17}$-*n*	−	−	−	−	−	−	−	−	−	−	+	+	+

By comparison of these data with those of the corresponding saturated acids containing the same number of carbon atoms[1b] it can be concluded that the presence of the olefin linkage has very little effect, if any, upon the bactericidal action. Moreover, the position of the olefin linkage in relation to the carboxyl appears to have no definite significance.

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[1] The previous two papers in this series are (a) Ford and Adams, XVI, THIS JOURNAL, 52, 1259 (1930); (b) Stanley, Jay and Adams, XV, *ibid.*, 51, 1261 (1929).

The allyl and undecenyl derivatives were made through the corresponding malonic esters. The α,β- unsaturated compounds were prepared by brominating the saturated acid, esterifying and then saponifying and eliminating hydrogen bromide.

Experimental

The details for preparing the proper halides, the substituted malonic esters and the monobasic acids can be found in the previous papers. The compounds containing the allyl and undecenyl groups were prepared by introducing the unsaturated groups second to the alkyl groups.

In producing the α,β-unsaturated acids, the acids were treated with bromine and phosphorus and the bromo acid bromides thus produced esterified directly with ethyl alcohol. The bromo esters were distilled under diminished pressure and then saponified with alcoholic potassium hydroxide.

α,β-Unsaturated Acids.--Organic acid (1 mole) was mixed with red phosphorus (0.33 mole) and bromine (1.8 mole) was run in slowly with vigorous stirring. After the initial reaction was over, the mixture was heated on a steam-bath for one-half to one hour. Upon cooling the separated material was filtered and absolute alcohol added slowly to the filtrate. After the reaction was over, the excess alcohol was removed on a steam-bath and the product washed with water, dried and distilled under diminished pressure. The ethyl a-bromo-di-n-heptyl acetate, b. p. 170–172° (2 mm.), ethyl a-bromo-di-n-butyl acetate, b. p. 102–104° (1.5 mm.), and ethyl a-bromo-di-n-octyl acetate, 179–181° (2 mm.), were obtained in this way.

A solution of 20% excess over two moles of potassium hydroxide dissolved in three to four times its weight of methyl alcohol was heated and the bromo ester slowly poured in. After several hours of refluxing the potassium bromide was filtered and most of the alcohol removed on a water pump. The potassium salt thus obtained was dissolved in water, steam was blown through to remove all alcohol and the solution then evaporated to dryness. Upon solution in water and pouring into excess hydrochloric acid, the free acid separated. It was extracted with ether, the ether removed and the acid purified by distillation under diminished pressure.

TABLE II

DIETHYL ALLYL ALKYL MALONATES

	B. p., °C.	n_D^{20}	d_4^{20}	Calculated, % C	Calculated, % H	Found, % C	Found, % H
$C_3H_5C(CO_2C_2H_5)_2C_9H_{19}$	144-146 (2 mm.)	1.4465	0 9469	69.88	10 50	69.21	10.43
$C_3H_5C(CO_2C_2H_5)_2C_{10}H_{21}$	154-155 (2 5 mm.)	1 4471	.9392	70.53	10.66	69 85	10.51
$C_3H_5C(CO_2C_2H_5)_2C_{11}H_{23}$	168-169 (5 mm.)	1.4478	.9345	71.18	10 73	71.10	10.61
$C_3H_5C(CO_2C_2H_5)_2C_{12}H_{25}$	166–168 (2.5 mm.)	1.4484	.9305	71.67	10.94	71.59	11.05
$C_3H_5C(CO_2C_2H_5)_2C_{13}H_{27}$	178–182 (5 mm.)	1 4499	,9276	72.19	11 07	72 04	10.91
$C_3H_5C(CO_2C_2H_5)_2C_{14}H_{29}$	184–186 (1.5 mm.)	1.4502	.9239	72.66	11.19	72.44	11 24

TABLE III

UNDECYLENYL ALKYL MALONIC ESTERS

	B. p., °C.	n_D^{20}	d_{20}^{20}	Calculated, % C	Calculated, % H	Found, % C	Found, % H
$C_{11}H_{21}C(CO_2C_2H_5)_2C_4H_9$	158–190 (4 mm)	1 4501	0 9206	71 67	10.94	71.90	11 02
$C_{11}H_{21}C(CO_2C_2H_5)_2C_5H_{11}$	190–194 (4 mm.)	1 4530	.9344	72.18	11.07	72.20	11.00
$C_{11}H_{21}C(CO_2C_2H_5)_2C_6H_{13}$	207-209 (4 mm.)	1 4514	9258	72 66	11 19	72 79	11.23
$C_{11}H_{21}C(CO_2C_2H_5)_2C_7H_{15}$	208-211 (4 mm.)	1.4518	,9225	73.10	11 29	73 00	11.12

TABLE IV

ALLYL ALKYL ACETIC ACIDS

	B. p., °C.	n_D^{20}	d_4^{20}	Calculated, %		Found, %	
				C	H	C	H
$C_3H_5CH(CO_2H)C_9H_{19}$	148–150 (3 mm.)	1.4510	0.9015	74.27	11.58	74.01	11.42
$C_3H_5CH(CO_2H)C_{10}H_{21}$	149–151 (1–1 5 mm.)	1 4520	.8989	74.93	11 75	74 75	11.38
$C_3H_5CH(CO_2H)C_{11}H_{23}$[a]	167–169 (4 mm.)	1.4530	.8953	75.69	11.81	75.30	11.78
$C_3H_5CH(CO_2H)C_{12}H_{25}$	164–166 (1–2 mm.)	1.4540	.8933	76 04	12.02	75.48	12.12
$C_3H_5CH(CO_2H)C_{13}H_{27}$[b]	179–183 (5 mm.)	1.4556	.8879	76.52	12.13	76.37	12.05
$C_3H_5CH(CO_2H)C_{14}H_{29}$	187–188 (2 5 mm.) (M. p. 24°)	1.4538 (at 25°)	.8865 (at 25°)	76.95	12.24	77.11	12.37

[a] This acid and the necessary intermediates were prepared by Marion S. Jay.

[b] This acid and the necessary intermediates were prepared by Wendell M. Stanley.

TABLE V

UNDECYLENYL ALKYL ACETIC ACIDS

	B. p., °C.		d_{20}^{20}	Calculated, %		Found, %	
				C	H	C	H
$C_{11}H_{21}C(CO_2C_2H_5)_2C_4H_9$	175–180 (3 mm)	1 4566	0.8929	76.04	12.02	76.23	11.96
$C_{11}H_{21}C(CO_2C_2H_5)_2C_5H_{11}$	186–190 (3 mm)	1.4575	.8956	76 52	12.14	75.98	11.98
$C_{11}H_{21}C(CO_2C_2H_5)_2C_6H_{13}$	200–204 (3 mm.)	1 4564	.8915	76.95	12 24	76.87	12.17
$C_{11}H_{21}C(CO_2C_2H_5)_2C_7H_{15}$	205–209 (5 mm.)	1.4572	.8870	77.34	12.34	77.23	12.38

TABLE VI

α,β-UNSATURATED DIALKYL ACETIC ACIDS

	B. p., °C.	n_D^{20}	d_{20}^{20}	Calculated, %		Found, %	
				C	H	C	H
$C_4H_9C(CO_2H)CHC_3H_7$	121–123 (2 mm.)	1.4484	0.9456	70.53	11.67	67.80	11.24
$C_7H_{15}C(CO_2H)CHC_6H_{13}$	180–182 (2 mm.)	1.4566	.8993	75.52	11 89	74.49	12.12
$C_8H_{17}C(CO_2H)CHC_7H_{15}$	185–186 (1 mm.)	1.4625	.8983	76.51	12.12	75.95	12.08

Summary

Various allyl alkyl acetic acids, undecenyl alkyl acetic acids and α,β-unsaturated acids have been prepared and tested for bactericidal action to B. Leprae. The unsaturated acids appear to be of about the same bactericidal value as the corresponding saturated acids.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS AND THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

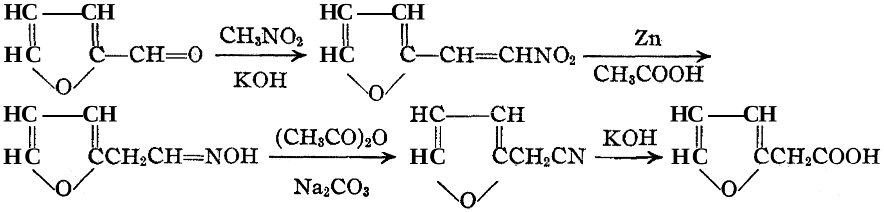
REARRANGEMENT OF THE ALPHA-FURFURYL GROUP. 2-FURYLACETIC ACID AND 5-METHYLFUROIC ACID

BY MABEL M. RUNDE, E. W. SCOTT AND JOHN R. JOHNSON

RECEIVED DECEMBER 7, 1929 PUBLISHED MARCH 6, 1930

During the past few years the chemistry of furan derivatives has been developed considerably due to the availability of pure furfural in large amounts. The furan analogs of many of the well-known benzene derivatives have been prepared and their properties investigated. The present work was undertaken with the object of synthesizing 2-furylacetic acid and a few related compounds.

The methods of synthesis which may be employed in the furan series are limited to some extent by the fact that furan and many of the simpler furan derivatives are relatively sensitive to strong mineral acids, particularly the halogen acids. For this reason it seemed advisable to devise a method for producing 2-furylacetic acid from furfural without using any reaction which involves such acids. The series of reactions indicated below was selected for this purpose and the desired product, 2-furylacetic acid, was obtained as a white crystalline solid, m. p. 67.3–67.5'.



Starting with a-furfuryl chloride, Kirner and Richter[1] recently synthesized an acid which was considered to be 2-furylacetic acid and described the substance as a white, crystalline solid which melted at 108.5–109.5°. A nitrile, supposedly 2-furylacetonitrile (a-furfuryl cyanide), was obtained by the action of α-furfuryl chloride upon an aqueous solution of sodium cyanide, and this was hydrolyzed by means of aqueous potassium hydroxide solution to the corresponding acid. The observation that the nitrile and the acid obtained by the method of synthesis used in the present work did not agree in physical properties with the compounds obtained from a-furfuryl chloride led to an investigation of the latter. The fact that 5-methylfuroic acid, a structural isomer of 2-furylacetic acid, is described in the literature as a white crystalline solid which melts at 108–109°,[2] suggested the possibility that a molecular rearrangement had occurred in the series of reactions involving a-furfuryl chloride. In order

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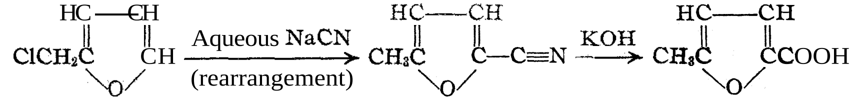
[1] Kirner and Richter, THIS JOURNAL, 51, 3131 (1929).

[2] Hill and Jennings, Am. Chem. J., 15, 167 (1893).

to test this point a specimen of authentic 5-methylfuroic acid was prepared by using as a starting material the methylpentose, rhamnose. The latter was converted into 5-methylfurfural by the usual method of ring closure, and the aldehyde was oxidized by means of silver oxide to the corresponding acid. The 5-methylfuroic acid obtained in this way had exactly the same melting point as the acid obtained by the method of Kirner and Richter from a-furfuryl chloride, and the melting point of a mixture of the two substances in equal amounts was exactly the same as that of the original pure substances. The identity of the acids was confirmed by microscopical studies of the crystals of both specimens.[3]

This result leads to the conclusion that a rearrangement of the a-furfuryl group into the 5-methylfuryl group occurred during one of the reactions involved in the synthesis of Kirner and Richter. It seems probable that this rearrangement takes place in the treatment of a-furfuryl chloride with aqueous sodium cyanide solution, so that the resulting nitrile is 5-methylfuronitrile and not 2-furylacetonitrile (a-furfuryl cyanide). Evidence in favor of this view is the fact that although the conditions for hydrolysis of the nitriles were practically the same in both syntheses, two different acids resulted. One might assume that rearrangement occurred in both cases or in only one, but it is more reasonable to suppose that rearrangement did not occur in either instance during the alkaline hydrolysis. It appears that the synthesis of Kirner and Richter follows the reactions given below.



α-Furfuryl chloride 5-Methylfuronitrile 5-Methylfuroic acid

The possibility that the chloride obtained from a-furfuryl alcohol[4] might not be a-furfuryl chloride but the isomeric 5-methyl-2-chlorofuran was also considered. The great reactivity of the chlorine atom in the chloride prepared from a-furfuryl alcohol makes this alternative quite unlikely, since one would not expect the chlorine atom of 5-methyl-2-chlorofuran to be highly reactive.[5]

In order to test the correctness of this view and to elucidate the mechanism of the rearrangement, further work is being carried on with the nitrile obtained from a-furfuryl chloride, and with other compounds that are

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[3] The authors wish to express their thanks to Professor C. W. Mason and Mr. P. P. McClellan for carrying out the microscopical studies reported in this paper.

[4] Kirner, THIS JOURNAL, 50, 1955 (1928).

[5] Investigations of the simple halogenated furans, such as 2-chloro-, 3-chloro-, 2-bromo- and 3-bromofuran, indicate that a chlorine or bromine atom attached to the furan ring is inert toward reagents that react quite readily with α-furfuryl chloride. The preparation and properties of the simple halogenated furans will be described in a forthcoming publication by Shepard, Winslow and Johnson.

obtained from this chloride by replacement reactions. The fact that α-furfuryl alcohol undergoes rearrangement in the course of ring opening in the presence of hydrochloric acid, with the formation of levulinic acid and methyl levulinate,[6] has a direct bearing on the rearrangement dealt with in the present work, since both rearrangements involve migration of a hydrogen from the carbon atom in the 5-position of the ring to the methylene group attached in the 2-position.

Experimental Part

Synthesis of 2-Furylacetic Acid

2-Furylacetaldoxime, $C_4H_3O—CH_2CH{=}NOH$.—Pure freshly distilled furfural was condensed with nitromethane according to the procedure of Thiele and Landers,[7] and the resulting furylnitroethylene was reduced by means of zinc and aqueous acetic acid as described by Bouveault and Wahl.[8] Since the purification of the oxime by distillation results in a considerable loss through decomposition, the crude oxime was converted directly into furylacetonitrile. The yields of the crude oxime were 65–70% of the calculated amount. Preliminary experiments indicated that the improved yield obtained by using the purified oxime did not compensate for the loss entailed in its purification.

2-Furylacetonitrile (a-Furfuryl Cyanide), $C_4H_3O—CH_2CN$.—The method employed for the dehydration of 2-furylacetaldoxime was similar to that used by Dollfus[9] for the conversion of phenylacetaldoxime into phenylacetonitrile. A trial experiment with the lower homolog of furylacetaldoxime, furfuraldoxime, indicated that the corresponding nitrile could be obtained in satisfactory yield by the use of this method. Fifty grams of crude 2-furylacetaldoxime (0.4 mole) was dissolved in 80 g. of acetic anhydride (0.8 mole) and the solution was boiled gently for two to three minutes. After cooling, the dark colored solution was poured carefully into a slight excess of aqueous sodium carbonate solution and the mixture was subjected to steam distillation. The 2-furylacetonitrile was extracted from the distillate with pure ether and the ethereal solution was dried over anhydrous calcium chloride. After removal of the solvent, the residual 2-furylacetonitrile was distilled under diminished pressure, b. p. 78–80°, at 20 mm. The yields were 5–6 g. (12–15%, calculated on the basis that the crude oxime was 100% pure).

2-Furylacetonitrile is a colorless liquid when freshly distilled but rapidly becomes yellow on standing, even in sealed tubes. It is appreciably soluble in water and is extremely soluble in alcohol and ether; it has a pleasant aromatic odor resembling that of phenylacetonitrile. The physical constants of the redistilled material were: b. p. 78–80° at 20 mm., n_D^{25} 1.4715, d_4^{25} 1.0854; MR_D (calcd.)[10] 28.24, MR_D (obs.) 27.60.

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[6] Pummerer and Gump, *Ber.*, 56, 999 (1923). These authors converted α-furfuryl alcohol into levulinic acid in 40% yields by heating with aqueous 0.5 N hydrochloric acid or 10% aqueous oxalic acid. In anhydrous methyl alcohol containing 0.1% of hydrogen chloride, a-furfuryl alcohol gave δ-methoxylevulinic acetal and methyl levulinate.

[7] Thiele and Landers, *Ann.*, 369, 303 (1909).

[8] Bouveault and Wahl, Bull. *soc. chim.*, [3] 29, 526 (1903).

[9] Dollfus, Ber., 25, 1917 (1892).

[10] The molecular refraction of this compound was calculated from the revised values of Eisenlohr for the atomic refractions [Landolt-Börnstein, "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 5th ed., Vol. II, 1923, p. 985]. The observed molecular refraction was obtained by the Lorentz-Lorenz formula.

Kirner and Richter reported the following physical constants for the nitrile obtained from α-furfuryl chloride, after four fractionations under diminished pressure: b. p. 74–75" at 27 mm., n_D^{20} 1.4833, d_4^{20} 1.04627; MR_D (calcd.)[11] 28.173; MR_D (obs.) 29.236.

Anal. Subs., 0.2243: CO_2, 0.5539; H_2O, 0.0944. Calcd. for C_6H_5ON: C, 67.27; H, 4.71. Found: C, 67.34; H, 4.71.

2-Furylacetic Acid, $C_4H_3O—CH_2COOH$.—The nitrile described above was hydrolyzed by refluxing for several hours with an 18% aqueous solution of potassium hydroxide. The resulting dark colored solution was cooled, treated with decolorizing charcoal and filtered. The filtrate was added slowly while stirring vigorously to a 20% excess of ice-cold 50% sulfuric acid which was covered with a layer of ether, in order to extract the organic acid from the aqueous layer as soon as it was liberated. The ethereal solution was separated, washed with a small volume of cold water and dried over anhydrous calcium chloride. After removal of the solvent the crude 2-furylacetic acid crystallized in yellow leaflets. After three crystallizations from petroleum ether, b. p. 25–40", the melting point remained constant at 67.3–67.5° (uncorr.), and the product formed beautiful glistening white leaflets. This acid is slightly soluble in petroleum ether, appreciably soluble in water, and very soluble in alcohol and ether.

Anal. Subs., 0.2054: CO_2, 0.4282; H_2O, 0.0877. Calcd. for $C_6H_6O_3$: C, 57.13; H, 4.80. Found: C, 57.35; H, 4.82. Neutralization value: calcd., 126.1; found. 125.2.

Microscopical Examination.—The substance can be crystallized from water or petroleum ether; both solvents give rise to the same crystal habit. Crystals from petroleum ether were used for this study.

The substance crystallizes in six-sided plates or in long thin tablets which in no way resemble needles. Examination shows these tablets to be elongated modifications of the six-sided plates. Edges of the crystals indicate the possibility of fine, lamellar twinning.

The angles at the ends of the crystals are about 122° with adjacent edges seldom of equal length. The crystals exhibit a very slight oblique extinction of between 2 and 3°, accompanied by dispersed, extinction. Birefringence is moderately weak. Due to the solubility of the substance in water and organic liquids, the indices of refraction could not be determined.

The interference figure indicates that the crystals are optically negative and that the observed crystal faces are perpendicular to a line drawn somewhere between the acute bisectrix and an optic axis, *i. e.*, they are inclined to the acute bisectrix. The optic axial angle was judged to be about 40° ($2V = 40°\pm$), assuming $n = 1.3$. The optic plane is nearly normal to the elongation direction of the crystals. Apparently, these belong either to the monoclinic or triclinic system.

Anilide of 2-Furylacetic Acid, $C_4H_3O—CH_2CONHC_6H_5$.—One gram of pure furylacetic acid was boiled gently with 3 g. of freshly distilled aniline in a small test-tube. The latter was provided with a cork bearing a small bent glass tube which allowed the water to distil out of the reaction mixture. After cooling, the contents of the tube

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[11] In a private communication Dr. Kirner stated that the value 30.571 which was published in his paper should be corrected to 28.173.

were treated with water and the product was taken up in ether. The ethereal solution was extracted successively with dilute hydrochloric acid and dilute potassium hydroxide solution to remove excess aniline and unreacted furylacetic acid. The solvent was distilled off and the residual anilide was crystallized from 50% alcohol. The purified 2-furylacetanilide formed grayish-white leaflets, m. p. 79–80° (uncorr.).

Anal. Subs., 0.1334: CO_2, 0.3468; H_2O, 0.0682. Calcd. for $C_{12}H_{11}O_2N$: C, 71.61; H, 5.51. Found: C, 70.90; H, 5.72.

Decarboxylation of 2-Furylacetic Acid. 2-Methylfuran.—In order to follow this reaction in an approximately quantitative way, a weighed sample of the acid was heated in a test-tube provided with a tared receiver and an ascarite bulb to absorb the evolved carbon dioxide. A slow stream of nitrogen was passed through the apparatus to displace the products of decomposition from the reaction tube. A sample of 2.009 g. of pure 2-furylacetic acid (0.0158 mole) on heating in an oil-bath at 250–260° for thirty minutes gave 0.559 g. of carbon dioxide (0.0127 mole) and 1.065 g. of 2-methylfuran (0.0130 mole). These quantities correspond, respectively, to 80 and 827, of the theoretical. The 2-methylfuran was dried over metallic sodium and redistilled; b. p. 62.8–63.5° at 737 mm. Wolff[12] reported b. p. 62.5–63° at 746 mm. for pure 2-methylfuran obtained by heating furfural hydrazone with sodium methylate.

Synthesis of 5-Methylfuroic Acid

Preparation from Rhamnose.—In a 1-liter flask connected through a short distilling column with condenser set for distillation, 50 g. of rhamnose was heated with 300 cc. of 10% hydrochloric acid containing 50 g. of sodium chloride. The methylfurfural steam distilled during the course of heating (one and one-half to two hours) and was extracted from the distillate with ether. The ether extract was washed with water and dried over anhydrous magnesium sulfate. After distilling off the solvent, the residual 5-methylfurfural (2.3–2.6 g.) was oxidized to the corresponding acid by means of silver oxide, in the presence of barium hydroxide.[13] The resulting 5-methylfuroic acid was crystallized twice from water, once from a mixture of benzene and petroleum benzine and finally from petroleum benzine, b. p. 100–110°; it formed white needles, m. p. 107–108.5" (108.3–109.8°, corr.).

Preparation from α-Furfuryl Alcohol.—The synthesis from a-furfuryl alcohol was effected through the preparation of α-furfuryl chloride,[4] reaction of the latter with aqueous sodium cyanide and hydrolysis of the resulting nitrile by means of 25% potassium hydroxide solution, according to the directions of Kirner and Richter.' The resulting acid was crystallized twice from water and twice from petroleum benzine, b. p. 100–110°; it formed white needles, m. p. 107–108.5" (108.3–109.8°, corr.). Kirner and Richter reported m. p. 108.5–109.5 (uncorr.).

The acid obtained in this way was mixed thoroughly with an equal quantity of the authentic 5-methylfuroic acid obtained from rhamnose and the mixture was found to melt at 107–108.5° (108.3–109.8°, corr.), which is exactly the same temperature as that of the original acids. The identity of the two specimens was confirmed further by a microscopical study of the crystals.

Microscopical Examination.—Both substances crystallize from water in the same crystal habit. The crystals are rectangular tablets or elongated six-sided tablets, the rectangular tablets being preponderant. Both types show beveled edges. Since the substances were soluble in water and most organic liquids, it was impossible to determine the refractive

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[12] Wolff, *Ann.*, *394*, 102 (1912).

[13] Delépine and Bonnet, Bull. *soc. chim.*, [4] 5, 883 (1909).

indices. The crystals exhibit strong birefringence and are either of the orthorhombic or the monoclinic system.

The rectangular tablets are perpendicular to the optic normal, as indicated by their interference figure, and show parallel extinction.

The six-sided tablets are perpendicular to the acute bisectrix and extinguish parallel to the elongation. This plane of extinction contains the axial plane. The crystals exhibit marked dispersion of the optic axes ($v > \rho$) and are optically negative. The apparent optic axial angle is greater than 120° ($2E > 120°$). The angles at opposite ends of the crystals are about 106° (determined, 105.5°, 106.2°).

Summary

1. 2-Furylacetic acid has been synthesized from furfural by a series of reactions which does not involve the use of mineral acids.

2. It has been shown that an acid prepared by the nitrile synthesis from α-furfuryl chloride, and described as 2-furylacetic acid, is actually the isomeric 5-methyl-2-furoic acid. It appears probable that rearrangement of the a-furfuryl group into the 5-methylfuryl group occurred in the reaction of a-furfuryl chloride with aqueous sodium cyanide solution.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS]

CERTAIN DIALKYL ACETIC ACIDS CONTAINING 12, 13 AND 14 CARBON ATOMS AND THEIR BACTERICIDAL ACTION TOWARD B. LEPRAE. XVIII[1,2]

BY B. F. ARMENDT AND ROGER ADAMS

RECEIVED DECEMBER 9, 1929 PUBLISHED MARCH 6, 1930

In a previous paper a comparison of a complete series of octadecanoic acids and a complete series of hexadecanoic acids of the general formula $RCH(CO_2H)R'$ were prepared in which R and R' were alkyl groups of the proper size to give the desired molecular weight. The various octadecanoic acids gave irregular bactericidal values but the hexadecanoic acids showed values which increased regularly as the carboxyl group was moved toward the middle of the chain. The conclusion was drawn that the bactericidal action was due to the particular physical properties of the acids and that among these properties molecular weight appeared to be very important. In several of the series of acids studied which contained a ring structure, compounds containing less than 16 carbon atoms were

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[1] Three previous papers in this field are XV, Stanley, Jay and Adams, THIS JOURNAL, 51, 1261 (1929); XVI, Ford and Adams, *ibid.*, 52, 1259 (1930); XVII, Browning, Woodrow and Adams, *ibid.*, 52, 1281 (1930).

[2] This communication is in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

invariably less or non-bactericidal. This investigation was undertaken to prepare a few representatives of the dialkyl acetic acids containing 12, 13 and 14 carbon atoms to compare them with those of higher molecular weight. The bacteriological results are given in Table I. The authors are indebted to Dr. W. M. Stanley for the bacteriological tests.

TABLE I

BACTERIOLOGICAL ACTION OF DIALKYL ACETIC ACIDS TO B. *Leprae*

		Dilutions of sodium salts in thousandths											
		5	15	25	50	62	74	85	100	125	155	192	250
C_{12}	*iso*-$C_3H_7CH(CO_2H)C_7H_{15}$	+	+	+	+	+	+	+	+	+	+	+	+
	$C_4H_9CH(CO_2H)C_6H_{13}$	+	+	+	+	+	+	+	+	+	+	+	+
	$C_5H_{11}CH(CO_2H)C_5H_{11}$	+	+	+	+	+	+	+	+	+	+	+	+
C_{13}	$C_4H_9CH(CO_2H)C_7H_{15}$	−	−	+	+	+	+	+	+	+	+	+	+
	$C_5H_{11}CH(CO_2H)C_6H_{13}$	−	−	+	+	+	+	+	+	+	+	+	+
C_{14}	$C_4H_9CH(CO_2H)C_8H_{17}$	−	−	−	−	±	−	*	*	+	+	+	+
	$C_5H_{11}CH(CO_2H)C_7H_{15}$	−	−	−	−	−	±	±	±	+	+	+	+
	$C_6H_{13}CH(CO_2H)C_6H_{13}$	−	−	−	−	−	±	±	−	±	+	+	+

It can be seen that the C_{12} acids are non-bactericidal, the C_{13} very slightly bactericidal and the C_{14} somewhat more. Even the C_{14} acids, however, are much lower in action than the C_{16} acids and somewhat less than the C_{18}, thus confirming the previous conclusion that molecular weight is an important factor.

The acids were all prepared by saponification of the proper disubstituted malonic esters.

TABLE II

DIETHYL DIALKYL MALONATES

Formula	B. p., °C.	d_4^{25}	n_D^{25}	Calculated, % C	Calculated, % H	Found, % C	Found, % H
Iso-$C_3H_7C(CO_2C_2H_5)_2C_7H_{15}$	137–140 (4 mm.)	0.9249	1.4375	67.94	10 74	09.70	11 33
$C_5H_{11}C(CO_2C_2H_5)_2C_5H_{11}$	147-149 (4 5 mm)	.9334	1.4343	67.94	10.74	67 60	10 80
$C_4H_9C(CO_2C_2H_5)_2C_6H_{13}$	143–147 (4 mm.)	.9333	1.4347	67.94	10 74	67 90	10 83
$C_4H_9C(CO_2C_2H_5)_2C_7H_{15}$	138–140 (3.5 mm)	.9288	1.4365	68 71	10 D0	68 70	11 20
$C_5H_{11}C(CO_2C_2H_5)_2C_6H_{13}$	146–149 (4 mm.)	.9300	1 4361	68.71	10 90	68 50	11 27
$C_4H_9C(CO_2C_2H_5)_2C_8H_{17}$	156–159 (4 mm)	,9263	1.4360	69 40	11.05	69 20	11 04
$C_5H_{11}C(CO_2C_2H_5)_2C_7H_{15}$	163 5–165 (5 mm.)	.9239	1 4371	69 40	11 05	69 80	11 37
$C_6H_{13}C(CO_2C_2H_5)_2C_6H_{13}$	155–158 (4 mm)	.9249	1 4373	69 40	11 05	69 70	10 90

TABLE III

DIALKYL ACETIC ACIDS

Formula	B. p., °C.	d_4^{20}	n_D^{20}	Calculated, % C	Calculated, % H	Found, % C	Found, % H
Iso-$C_3H_7CH(CO_2H)C_7H_{15}$	133–134 (4 mm)	0 9429	1 4399	71 92	12.07	71.70	12.05
$C_5H_{11}CH(CO_2H)C_5H_{11}$	141–143 (4 mm)	.8900	1.4381	71.92	12 07	71.03	12 16
$C_4H_9CH(CO_2H)C_6H_{13}$	134–135 (4 mm)	.8945	1 4391	71.92	12.07	71 67	12 02
$C_4H_9CH(CO_2H)C_7H_{15}$[a]	148–149 (3 mm)	.8911	1 4409	72.80	12 23	72.55	12 43
$C_5H_{11}CH(CO_2H)C_6H_{13}$	149–150 (4 mm)	8850	1 4410	72 80	12.23	72 31	12 14
$C_4H_9CH(CO_2H)C_8H_{17}$	160–161 (4 mm.)	8873	14435	73.60	12.36	73.25	12 42
$C_5H_{11}CH(CO_2H)C_7H_{15}$	155.5–157 (4 mm)	8900	1.4430	73 60	12.36	73 50	12 10
$C_6H_{13}CH(CO_2H)C_6H_{13}$	159–160 (4 mm.)	8805	1 4421	73 60	12 36	73 45	12 23

[a] Levene and Taylor, J. *Biol.* Chem., 54, 351 (1922), report the constants b p, 179° (13 mm.), d_4^{20} 0.8860, n_D^{20} 14403 and on the ester as b p. 177–178° (12 mm.), d_4^{20} 0.9318, n_D^{20} **1.4366.**

Experimental

The general methods of preparation of the various intermediates have been described in previous articles in this series.

Summary

1. A number of dialkyl acetic acids having 12, 13 and 14 carbon atoms in the acid molecule have been prepared and tested for bactericidal action toward B. *Leprae*.

2. The dodecanoic acids have no bactericidal action, the tridecanoic acids practically no action, and the tetradecanoic acids have slight bactericidal action. This indicates as in previous researches that the molecular weight of the molecule plays an important role.

URBANA, ILLINOIS

[CONTRIBUTION BROM THE CHEMICAL LABORATORY OF THE UPJOHN COMPANY]

MICRO-DETERMINATION OF SULFUR BY FUSION

BY HAROLD EMERSON

RECEIVED DECEMBER 13,1929 PUBLISHED MARCH 6, 1930

In the course of several sulfur determinations by the Pregl method, the question was raised as to the possibility of finding a method which would require less apparatus and manipulation.

The method of Récsei[1] was unsatisfactory because of the tendency of sodium peroxide to deteriorate on standing, also the danger accompanying the use of it, the action at times taking place with explosive violence. It was found that the macro method employing potassium nitrate as an oxidizing agent could be modified for use as a micro method.

Experimental

Prepare the fusion mixture by mixing four parts by weight of sodium carbonate and three parts of potassium nitrate and grinding the mixture to a fine powder. This can be kept indefinitely.

Weigh a finely powdered sample equivalent to approximately 0.5 mg. of sulfur and mix thoroughly with 100 times its weight of the fusion mixture in a 20-cc. nickel crucible. Sprinkle a thin layer of the mixture over the top to prevent sulfur fumes from escaping. Place a close-fitting cover on the crucible and set it in a porcelain crucible of convenient size.

With a Bunsen burner apply a very low flame, gradually increasing it during ten minutes until the maximum is reached. Continue heating for fifteen minutes, then shut off the flame and allow the crucible to cool.

Dissolve the contents of the crucible in 5 cc. of warm water and filter into a 30-cc. beaker. Wash the crucible and filter with 10 cc. more water and add to the solution. Acidify with hydrochloric acid and heat to boiling.

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[1] Andor Récsei, *Chem.-Ztg.*, **50**, 785 (1926).

Precipitate with 1 cc. of a 10% solution of barium chloride and let the mixture stand for at least one hour, after which the precipitated barium sulfate may be weighed on a micro Neubauer crucible. To prepare the crucible, wash it with chromic acid and water and then, after closing the crucible with the lid and lower cap, ignite it on a crucible cover and weigh when cool.

Filter the precipitate in the same manner as with a Gooch crucible in the macro method and again ignite and weigh the crucible as before. A few results are given in Table I.

TABLE I

PERCENTAGE OF SULFUR IN ORGANIC COMPOUNDS

Compound	Sample, mg.		$BaSO_4$, mg.		Sulfur, %		
					Calcd.	Found	
Cystine	4.472	7.039	8.516	13.412	26.06	26.15	26.16
Methyl orange	9.125	6.988	6.390	4.910	9.8	9.62	9.65
Aminonaphthol sulfonic acid	5.807	6.698	5.729	6.646	13.47	13.55	13.62
Thymol blue	8.230	8.698	3.960	4.185	6.87	6.61	6.61
Potassium methyl sulfonate	4.646	7.200	8.152	12.562	23.89	24.09	23.96
Sulfanilic acid	5.604	5.366	7.598	7.243	18.52	18.62	18.53

Summary

By this method the sulfur content of any sample can be determined very accurately. It requires very little manipulation and apparatus and is economical in respect to time and material.

KALAMAZOO, MICHIGAN

NEW BOOKS

Physikalisch-chemisches Praktikum. (Laboratory Manual of Physical Chemistry.) By Professor Dr. K. FAJANS, and Dr. J. WÜST, of the University of Munich. Akademische Verlagsgesellschaft m. b. H., Schlossgasse 9, Leipzig C 1, Germany, 1929. xvi + 217 pp. 74 figs. 16 X 24 cm. Price, unbound, M. 12; bound, M. 13.50.

The outstanding feature of this laboratory manual is the great variety of experiments presented. In addition to the experiments commonly found in laboratory guides, we have here chapters on Adsorption from Solution, Coagulation of Sols by Electrolytes, Metallography, Rate of Radioactive Disintegration, Adsorption of Light, Ultraviolet Spectroscopy, Electrochemical Preparations and the Lead Accumulator. The experiments are not as formidable as this array of topics might suggest, being carried out for the most part with quite simple apparatus.

The experiments have been used at the Munich laboratory for the most part, the rest having been tested at Würzburg, Karlsruhe, or Erlangen. The volume contains sufficient material to occupy a student's entire time for one semester. Each chapter begins with a theoretical discussion, complete enough to enable the student to understand the experiment.

The apparatus is in most cases illustrated and carefully described, making the book in all as nearly self-teaching as one could wish.

The volume should be most welcome to those who are interested in introducing new material into the laboratory work in physical chemistry.

HENRY E. BENT

Leipziger Vorträge 1929: Dipolmomente und chemische Struktur. (Leipzig Lectures 1929: Dipole Moments and Chemical Structure.) Edited **by P. DEBYE. S. Hirzel, Leipzig, 1929. viii + 134 pp. 35 figs.** and 1 plate. **14.5 X 22 cm. Price, RM. 9.00.**

The papers presented at Leipzig last summer, in the course of a symposium on the electric moments of molecules, have been reprinted in this volume, together with a short preface by Professor Debye. They form a stimulating account of the more recent applications of this magnitude to the problems of molecular structure. Those who are engaged in the measurement or in the interpretation of dipole moments will find numerous points of interest in Sanger's report of the investigation of further compounds by means of a study of the temperature change in the dielectric constants of their vapors, in Estermann's description of the method of molecular rays and in the measurements of the dielectric constants of dilute benzene solutions of heptane derivatives reported by Errera and Sherrill. The specialist in this field will also be interested in the papers of Errera on the changes of the polarization of polar substances with concentration and temperature, on molecular associations and on the atomic polarization of crystals. The ultraviolet absorption spectra of some disubstituted benzenes have been measured by Wolf, and Höjendahl has given a discussion of the forces in regular crystals.

Of much more general interest to chemists, however, are the applications to chemical problems. Perhaps the greatest advance has been made in relating the dipole moment to the structure of the molecule. Errera has given a full discussion of this subject showing, in particular, how the electric moment may be used for the identification of isomers. In a paper by Ebert the fundamental postulates of organic chemistry are analyzed in the light of recent physical experiments. The relation between the Kerr effect and the molecular structure has been discussed by Wolf, and the possible means of attacking the problems of reaction velocity from a consideration of the polar properties of the molecules have been developed by Hiickel. The attitude of the theoretical physicist toward the problem as a whole is given by Hund.

Taken as a whole the book affords a ready means by which chemists may familiarize themselves with this relatively new method of investigation and with the results that have been obtained by its use. Admittedly these results are as yet meager, but it may be hoped with a fair degree of confidence that they will be greatly extended in the near future. The articles collected in this volume contain much that shows the necessity for further work along these lines.

HUGH M. SMALLWOOD

The Chemical Effects of Alpha Particles and Electrons. By SAMUEL C. LIND, Ph.D., Director of the School of Chemistry, University of Minnesota. Second edition. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York. 252 pp. 13 figs. 15 × 23.5 cm. Price, $5.00.

The success of the American Chemical Society Monograph Series is evident from the long list of those published, but the most striking proof is the issuance of successful revised editions of those scholarly earlier monographs which probably would not have been published at all without the aid of the American Chemical Society. Dr. Lind has brought his book up to date by omitting the sections on isotopes (in deference to Aston's monograph), by expanding to eleven chapters the four devoted to kinetics and the relationships between radiochemical effects, and by a careful revision of each paragraph to accord with the intervening research results. Since the first edition was itself the stimulant for a large part of this research, the result is a much more unified and clearer presentation. The thirty per cent. increase in size constitutes obvious justification for the first edition as well as for the second.

G. L. WENDT

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[CONTRIBUTION FROM THE COLLOID LABORATORY, UNIVERSITY OF WISCONSIN]

THE STRUCTURE OF GELATIN GELS FROM STUDIES OF DIFFUSION[1]

BY LEO FRIEDMAN[1a] AND E. O. KRAEMER

RECEIVED JUNE 10, 1929 PUBLISHED APRIL 7, 1930

The behavior and properties of gelatin systems have been the subject of a good deal of study by colloid investigators because they serve as a prototype of gel-like bodies occurring in living organisms. Further studies into the mechanism and necessary conditions for gel formation, the structure and characteristic properties of gels, and the changes in state which gels undergo should throw much light onto related biological problems.

In general, gel formation may be considered to be an unsuccessful or incomplete precipitation of a solid phase from a liquid system, and it is always preceded by the sol form. The rigidity and elasticity of a gel is due to the presence of a solid or semi-solid phase, which in some gels is indicated by ultramicroscopic observations and by the marked Tyndall effect; but gelatin gels can be prepared that show no structure in the ultramicroscope nor any Tyndall effect. This and the general behavior of gelatin gels indicate a very fine grained structure. The high vapor pressure of water above a weak gel and the permeability to ions and molecules show that on a molecular scale the gel does not possess the elasticity and rigidity that it exhibits in bulk.

By assuming gelatin gels to consist of threads or short chains loosely knit together in three dimensions, Kraemer[1b] calculated the average value of the interval between two threads. By such an approximation he found this to be of the order of magnitude of 100 millimicrons in a very dilute gel.

It was the purpose of this investigation to study further the micro-structure of gelatin gels and the order of magnitude of the discontinuities within them. Attempts to study directly the micro-structure of weak

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[1] The substance of this article was included in a paper presented at the Midwest Regional Meeting of the American Chemical Society, University of Chicago, May 27 and 28, 1927.

[1a] An extract from a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Wisconsin.

[1b] Kraemer, J. Phys. *Chem.*, **19, 1523 (192.5).**

gelatin gels have been very few. Bachmann's[2] ultramicroscopic observations of gelatin gel formation are perhaps not so significant, because it is possible to prepare gelatin gels which show no structure in the ultramicroscope. Freundlich and Seifriz[3] investigated the micro-rigidity and elasticity of weak gels by observing the behavior of small nickel particles in a magnetic field. It was found that on a micro scale the rigidity and elasticity of gelatin gels are far from uniform.

In order to decrease the scale of observation still further, Kraemer,[4] by means of the cinematograph, studied the Brownian motion of very small mercury particles imbedded in a weak gel. From these observations it appears that the structure of weak gelatin gels is even considerably finer than the indicating mercury particles and their displacements.

None of the above techniques enable one to detect the heterogeneities of these weak gelatin gels, for the magnitude of the structural units lies somewhere between the scale of Brownian motion experiments and the molecular size. The purpose of this investigation was to explore this particular region by the study of the diffusion of molecules into and through gels. It was sought to give a detailed and quantitative interpretation of diffusion data in terms of heterogeneous gel structure and the possible dimensions of the pores.

As has been pointed out by Miss Lloyd,[5] investigations into gel structure should be carried out in systems uncomplicated by ionic reactions present in aqueous solutions. In this research it was attempted to conform with her suggestion as much as possible, by using only electrodialyzed materials free from electrolytes, while still working in aqueous solution. In this way it was hoped to observe the gel properties and not the influence of electrolytes on these properties.

Method for Study of Diffusion in Gels.—In search of more exact values of diffusion constants in gels than can be obtained by the methods described in the literature,[6] a method was developed which has many advantages over those previously used. A mass M of material was uniformly distributed at time zero in a gel of depth a. This gel was covered with an equal depth of water which was kept continually stirred. The material diffused through the gel and into the water, where its concentration was determined as a function of the time by analysis of very small

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[2] Bachmann, *Z. anorg. Chem.*, *73*, 125 (1911).

[3] Freundlich and Seifriz, *Z. physik. Chem.*, 104, 233 (1923).

[4] Kraemer, "Colloid Symposium Monograph," 1924.

[5] Alexander, "Colloid Chemistry," Chemical Catalog Co., New York, 1926, Vol. I, p. 781.

[6] (a) Graham, Ann., 121, 5, 29, 36 (1862); (b) Bechhold and Ziegler, *Z. physik. Chem.*, 56, 105 (1906); (c) Herzog and Polotsky, *ibid.*, 87, 449 (1914); (d) Stiles and Adair, *Biochem.* J., 15, 621 (1921); (e) Stiles, *Proc. Roy. Soc.* (London), 103A, 261 (1923); (f) Fricke, *Z. Elektrochem.*, 31, 430 (1925).

samples by means of the Zeiss Immersion Refractometer. More often the system was reversed, in which case the mass of diffusing material was in the water at the beginning of the experiment and the rate at which it diffused into the gel was measured. Since at infinite time, if no reaction took place between the gel and the material diffusing, half of this material would be in the gel and half in the water, it made no difference which system was used.

In this method it was not necessary to avoid convection currents due to light and vibration, as is the case in systems where a liquid column is supposed to remain undisturbed. Diffusion took place more rapidly than in systems previously described in the literature, because here the maximum possible concentration gradient was always maintained at the interface. In one experiment lasting as little as four days it was possible to obtain 10 or 12 values of the diffusion constant from the same system, which showed any variation or steady shift that had taken place with time, and gave a "best value" which was the mean of 10 or 12. By introducing a third substance into the preliminary soaking bath where a swelling equilibrium was supposed to be attained, an equilibrium with respect to this third material could also be reached, and its effect upon the diffusion process studied. Since no warm solution was ever poured upon the gel after it had set, no melting could take place at the diffusion boundary, and a sharp interface was maintained. No precipitation was taking place, therefore diffusion was not being hindered by clogging in the pores of the gel. These advantages, coupled with the accurate analysis possible by use of the Immersion Refractometer, made this method capable of very exact results. This system was, however, of no use for the study of diffusion in very concentrated or very dilute gels, for the former would swell too much after diffusion had started and the stirring would tear the surface of the weak gels.

Description of Apparatus.—The experimental determinations of the diffusion constants were carried out in ordinary wide-mouthed glass bottles with a capacity of 500 cc. and of known cross sectional area. The aqueous layer above the gel was constantly and uniformly stirred by small glass stirrers, thus keeping the concentration of diffusing material at the top surface of the gel the same as that of the whole layer. A capillary pipet was used to extract two or three drop samples of the solution above the gel. During the determinations the bottles were supported in a thermostat kept at the desired temperature. The Zeiss Immersion Refractometer equipped with auxiliary prisms was used to determine the concentration of diffusing material in the aqueous layer. Only two or three drops of the liquid were necessary and the analysis was correct to within ±0.01% of the material.

Experimental Procedure

The purified gelatin was diluted to approximately the desired concentration, cooled to 5°, cut into small pieces and allowed to soak in water at 5° for a long enough period to reach a swelling equilibrium. Then the water was drained off and saved for future

use while the gelatin was again melted. In some of the work it was found unnecessary to go through this preliminary soaking treatment, as the gels showed no tendency to change volume during diffusion. Measurements were made with a depth gage at the start and the end of the experiments to be certain that the changes in volume of the gel were small enough to be of no influence on the results. In five tests the maximum change was 0.08 cm. and the mean 0.04 cm. while the total depth of gel was about 5 cm. Two hundred cc. of molten gelatin was poured into a calibrated bottle and this was placed in the thermostat at 5°. In order to prevent hardening of the surface, the gel, as soon as it had set, was covered with a little of the water that had been saved. After twenty-four hours, a time which was found sufficient for the system to reach a gelling equilibrium, the water was removed and the gel covered with 200 cc. of a solution of non-electrolyte.

The refractometer readings for water and the non-electrolyte solution were known. In order to determine the amount of non-electrolyte that had diffused into the gel as a function of the time, refractometer readings of the solution were taken from time to time during the experiment. When the original water was stirred in contact with the gel as a blank experiment, the refractive index remained constant for the length of the test (seventy-six hours). In some of the earlier work the diffusing substance was placed in the gel and allowed to diffuse out into pure water. Results obtained from this type of system gave practically the same constants as for the reversed system, as can be seen by study of Fig. 2 and Table III (d). The determinations marked with an asterisk show results for diffusion from the gel, the others into the gel. These are plotted together in Curve d, Fig. 2. When it was desired to study the effect of a third material on the diffusion process, this was introduced into the gelatin and the water before the preliminary soaking treatment and an equilibrium for this material thus obtained before the diffusate was added.

Calculation of the Diffusion Constant.—The equation connecting the coefficient of diffusion with the time concentration data in the liquid layer was derived for this system from an entirely theoretical standpoint by Dr. W. Weaver, mathematical physicist, University of Wisconsin.? This equation may be put in the form

$$V = {}^1/_2 - \Sigma \frac{8}{(2\,n + 1)^2\pi^2}\, e^{-(2n + 1)^2 \frac{\pi^2}{4} T}$$

where V is the fraction of the material that has diffused into the gel per unit of area, starting with all the material in the liquid layer, and $T = kt/a^2$, where k is the coefficient of diffusion, t is the time in seconds, and a is the depth of the gel layer and also that of the liquid. In order to use this series, it was expanded to twelve terms.

Substituting into this equation values for T and solving for V, it is possible to plot the theoretical curve shown in Fig. 1. In actual use, in order to obtain greater accuracy, this curve was cut up into small segments, each plotted on a separate sheet. To determine the diffusion coefficient, k, for any sample of gel, the value of T corresponding to the experimentally determined value of V was read from this theoretical curve. k can then be calculated from the previously mentioned relation $k = a^2T/t$. In this way a value of the diffusion coefficient was obtained from each

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[7] Weaver, Phys. Rev., 31, 1072 (1928)

determination of the concentration of the aqueous layer and the mean value of 10 or 12 such determinations was used as the "best value."

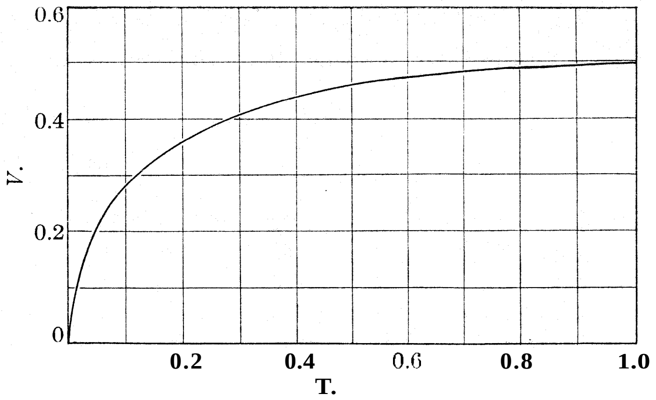

Fig. 1.—Theoretical diffusion curve.

The details of the calculation can best be shown by giving the data and calculations for one of the experiments on the diffusion of sucrose into a gelatin gel, Table I. Diffusion took place from a 5% sucrose solution into a 6.91% gel at a temperature of 5°. The total shift of the refractometer reading from that of water caused by the sucrose in the solution at zero time was 19.17. The refractometer shifts listed in Column 2 are shifts from the reading of the aqueous solution at zero time and represent the amount of sucrose that had left the liquid and penetrated into the gel. V, the fraction of sucrose that had penetrated into the gel, was obtained by dividing the shift given in the second column by the total shift 19.17. It was not necessary to change refractometer readings to concentrations by means of calibration curves, for over the range of concentrations used

TABLE I

DIFFUSION OF SUCROSE IN A GELATIN GEL

Time in hours	Refractometer shift	V	T	$K \times 10^5$
8.55	0.98	0.0511	0.00228	0.154
21.08	1.49	.0777	.00538	.149
29.77	1.74	.0908	.00752	.148
45.42	2.01	.1048	.01025	.132
53.90	2.24	.1169	.01305	.142
70.50	2.57	.1340	.01785	.148
79.25	2.68	.1397	.01945	.144
93.90	2.97	.1549	.02450	.153
117.20	3.26	.1700	.03050	.152
144.87	3.65	.1904	.03990	.161
Area of bottle = 43.59 sq. cm.			Mean =	0.148

there was *a* linear relation between these two, Values for T and K were obtained as described above.

Table II shows, for several experiments, the maximum and average deviations of any one value from the mean and the accuracy of the check that can be obtained for duplicate experiments by this method.

TABLE II

DIFFUSION IN GELATIN GELS

Diffusing substance	Gel concn., %	Diffusion constants ($K \times 10^5$) Expts.	Max.	Min.	Mean	Max. dev., %	Av. dev., %	Variation of mean, %
Sucrose	6.9	10	0.161	0.132	0.148	10.8	3.7	
Urea	2.65	6	.807	.693	.744	8.5	3.9	
Urea	2.65	6	.794	.685	.740	8.8	3.5	0.5
Urea	2.9	6	.718	.590	.645	11.3	5.9	
Urea	2.9	6	.681	.617	.644	5.7	3.6	0.2
Urea	4.0	7	.584	.477	.541	11.8	6.1	
Urea	4.0	7	.598	.437	.539	18.9	6.9	0.4

Diffusion of Non-Electrolytes in Gelatin Gels.—The gelatin used in these studies was purified by soaking in $N/128$ acetic acid and water, and finally by electrodialysis. The purified gelatin obtained in this way had an ash content of 0.1% or less. In order to show the effect of concentration of gelatin upon the structure of the gels, determinations of the rates of diffusion of 3 non-electrolytes, urea, glycerin and sucrose, were made in various concentrations of gels. Curve a, Fig. 2, shows the results for diffusion of urea from a gelatin gel (Silver Label Gelatin) where the gel originally contained 6% of urea. A decrease in the rate of diffusion of 20% as the concentration of gel increased from 2.5 to 5% is shown, contrary to the statement by Stiles and Adair[6d] that above 2% there is very little change. It is probable that below 2% the line would bend upward and cut the zero axis at the diffusion constant for water. It was, however, impossible to work with such dilute systems by the method used in this investigation.

Curve b also shows the diffusion of urea from gels (Silver Label Gelatin) originally containing 6% of urea. The slope of the line here is different from that in Curve a, as would be expected, since the gelatin used was from a different supply and had been subjected to different preliminary treatment. It is impossible to prepare two samples of gelatin to give comparable diffusion results unless material from the same source, purified under the same conditions and given exactly the same previous heat treatment is used. In all cases, data used for any one curve or given in any table for comparison were obtained from gelatin from one large stock supply of purified material and from samples treated in exactly similar manner.

Curve c shows the diffusion of urea into gels (gelatin for this and all following work was of calf skin stock supplied by the U. S. Gelatin Company) from a 3% urea solution. The line would intercept the axis for zero diffusion at a concentration of about 30%, so an attempt was made to see whether diffusion were truly zero at this concentration of gelatin. The results are shown in Part c, Table III. The gel used cannot be compared to the others, for it was an unpurified gel. The remarkably high value,

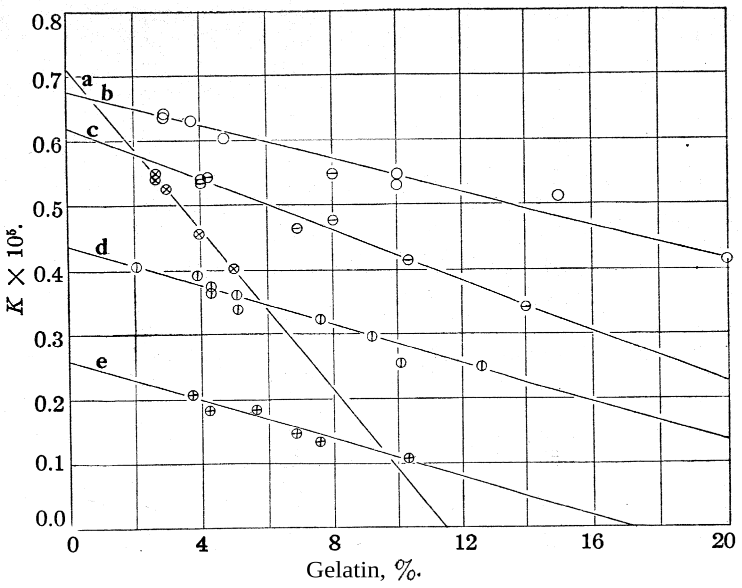

Fig. 2.—Diffusion in gelatin gels.

TABLE III

DIFFUSION IN GELATIN GELS *vs.* CONCENTRATION OF GEL

Gelatin concn., %	Total diff., hours	Expts.	Diff. constants ($K \times 10^5$) Max.	Min.	Mean
		(a) 6% Urea from gel			
2.65	137	6	0.807	0.693	0.744
2.65	137	6	.794	.685	.740
3.0	94	4	.758	.709	.725
4.0	118	5	.689	.617	.657
5.0	118	5	.625	.585	.604
		(b) 6% Urea from gel			
2.9	107	6	.718	.590	.645
2.9	107	6	.681	.617	.644
3.7	107	6	.658	.615	.637
4.7	107	6	.664	.560	.608
10.0	112	5	.603	.469	.533
10.0	112	4	.578	.530	.550
15.0	112	5	.554	.436	.513
20.0	112	5	.456	.362	.416

TABLE III (*Concluded*)

Gelatin concn., %	Total diff., hours	Expts.	Diff. constants ($K \times 10^5$) Max.	Min	Mean
			(c) Urea into gel from 3% solution		
4.0	107	7	.584	.477	.541
4.0	108	7	.598	.437	.539
4.2	65	5	.618	.506	.547
6.9	120	8	.522	.400	.468
8.0	111	8	.655	.410	.549
8.0	113	9	.581	.407	.479
10.35	146	9	.483	.363	.419
14.0	110	8	.390	.280	.347
29.8	25	3	.387	.228	.320
			(d) Glycerin into gel from 3% solution		
2.0*	209	15	.462	.354	.406
3.8	71	6	.415	.363	.390
4.2	69	6	.403	.314	.364
4.2	122	11	.421	.287	.373
5.0	97	4	.351	.324	.338
5.0*	255	13	.460	.287	.362
7.5*	255	15	.443	.210	.323
9.1	94	7	.327	.237	.296
10.0"	135	7	.271	,231	.253
12.5"	255	12	.301	.187	.249
			(e) Sucrose into gel from 5% solution		
3.8	216	8	.264	.144	.209
4.3	144	13	.213	.145	.184
5.7	94	8	.205	.167	.186
6.9	145	10	.161	.132	.148
7.6	81	5	.151	.124	.135
10.35	145	10	.110	.098	.107
			(f) Sucrose into gel from 3% solution		
28.8	48	6	.037	.025	.032
			(g) Lactose into gel from 3% solution		
25.0	29	2	.038	,035	.037

however, for the diffusion constant would indicate that diffusion does not cease at this concentration. This would be expected if diffusion takes place through capillaries of many sizes and the diffusion constant is a measure of the average.

Curve d shows the course of the diffusion of glycerin in various concentrations of gels. Curve e shows the diffusion of sucrose into gels, the results being in good agreement with those for the diffusion of urea and glycerin.

Using sucrose and lactose, larger molecules than urea, another attempt was made to see whether diffusion would be zero in gels so concentrated that Curve e would indicate no diffusion. The results are shown in Parts f and g of Table III and, although diffusion is very slow, there is no question that some of the material is penetrating the gel.

Dimensions of the Gel Framework.—As shown by the curves in Fig. 2, diffusion is considerably slower in a gelatin gel than in pure water. The diffusion coefficient for urea in water at 5° as calculated from Öholm's[8] data is 0.880×10^{-5}, that for glycerin is 0.552×10^{-5} and for sucrose 0.285×10^{-5}. The two phase solid–liquid theory best explains the results obtained in this investigation. If it is assumed that this theory is correct, and that diffusion takes place through the liquid in the pores of the gel, this slowing down of diffusion may be due to three different causes. First, the solid gelatin in the gel mechanically blocks part of the area across which diffusion can take place; second, since the diffusion is taking place through very tiny capillaries, there will be a drag on the molecules due to the proximity of the solid walls; and third, the viscosity of the liquid in the gel is different from that of water at the same temperature. This last factor also includes any specific attraction of the gel material for the diffusing substance.

To take care of these three influences, the following relation was set up:

$$K_{\text{water}} = K_{\text{gel}}\,(1 + 2.4r/R)(1 + \alpha)(1 + \pi)$$

where r is the radius of the diffusing molecule, R is the average radius of the pores in the gel, α is the correction factor for the viscosity and π is the correction factor for the mechanical blocking. At zero concentration of gelatin the difference between the diffusion constants in pure water and the extrapolated values for the gelatin is due only to the difference in viscosity of the liquids through which diffusion takes place and any specific action. Therefore the correction factor α can be calculated from these values of the diffusion constant. The correction for mechanical blocking was calculated from the formula given by Dumanski[9]

$$\pi = \sqrt[3]{(g/d)^2}$$

where g is the number of grams of gelatin in 1 cc. and d is the density of the gelatin or the inverse of the partial specific volume. The correction factor $(1 + 2.4r/R)$ is the best approximation that can be obtained for the size of the pores. It is from Ladenburg's correction for the fall of bodies in capillary tubes and was originally intended to be applied to Stokes' law.

TABLE IV

SIZE OF THE PORES IN A GELATIN GEL

Substance diffusing		Sucrose	Glycerin	Urea	Naphthol Yellow S
Radius of the pores in millimicrons	5% gel	5.5	5.7	4.7	0.8 (Herzog and
	10% gel	1.4	1.7	1.5	... Polotsky)
	15% gel	0.5	1.0	0.8	...

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[8] Öholm, *Medd. Vetenskapsakad. Nobelinst.*, 2, n23; Öholm, *Z. physik. Chem.*, **70**, 399,401 (1909).

[9] Dumanski, *Kolloid-Z.*, **3**, 210 (1908).

The correction has been used by Westgren and Nordlung and found to hold very well. The radii of the diffusing particles were determined by calculation from Einstein's formula

$$D = \frac{RT}{N}\frac{1}{6\pi \eta r}$$

Using Curves c, d and e of Fig. 2 and the values from Öholm given above, calculations were carried out in this manner and the results shown in Table IV were obtained.

The following values for the diffusion of the dye Napthol Yellow S were taken from the work of Herzog and Polotsky.[10]

In water at 7.3 °C., $K \times 10^5 = 0.468$
In 5% gelatin gel at 1.2° $= 0.148$

Using these values for the calculations outlined above' a value of **0.83** mμ was found for the radius of the pores in their gel. This is in excellent agreement with this investigation; a difference of this magnitude would be expected because of the difference in gelatin used and the greater adsorption of diffusate.

Summary

1. A new method for the study of diffusion rates in gels has been described and its advantages pointed out.

2. An equation connecting the time–concentration data with the diffusion constant has been presented and its use described.

3. The data and calculations presented show the method to be capable of a degree of accuracy of about 1%.

4. It has been shown that a very marked decrease in the rate of diffusion in gelatin gels is brought about by increase of concentration of the gel.

5. A relation has been set up connecting the diffusion constants in water and in gel in such a manner as to include the radii of the openings in the gel framework.

6. Calculations have been made of the size of these openings in the gel framework for 5, 10 and **15%** gels from the results of diffusion experiments with urea, glycerin and sucrose.

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[10] Freundlich, "Colloid and Capillary Chemistry," 1926, p. 549.

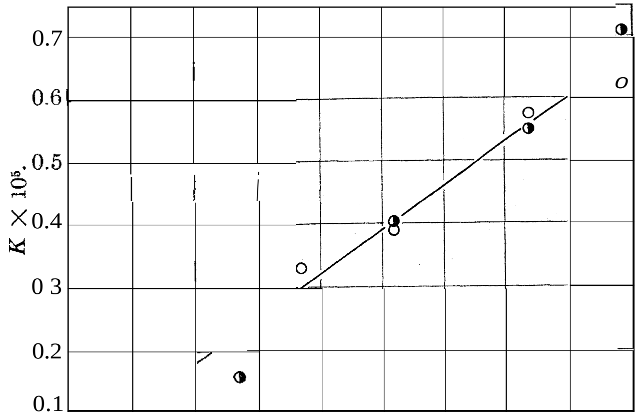
[CONTRIBUTION FROM THE COLLOID LABORATORY, UNIVERSITY OF WISCONSIN]

DIFFUSION OF NON-ELECTROLYTES IN GELATIN GELS[1]

BY LEO FRIEDMAN

RECEIVED JUNE 10, 1929 PUBLISHED APRIL 7, 1930

It was desired to investigate the diffusion in gels of materials with various molecular weights in order to determine whether the process followed the laws of diffusion or if it was specific for each diffusion substance regardless of the size of the molecule. If the former is true, then the product of the molecular weight and the square of the coefficient of diffusion should be a constant and the relation between the coefficient and the inverse of the square root of the molecular weight should be a straight line. The method of diffusion analysis described in a previous paper by Friedman and Kraemer was used.[1a]



Mol. wt. of diffusant.

○, Uncorrected; ◑, corrected.

Pig. 1.—Diffusion of non-electrolytes in a gelatin gel.

Experiments with several non-electrolytes showed that there was considerable variation from the relation mentioned above. An investigation of the effect of these non-electrolytes upon the diffusion process in gels was then carried out in an attempt to determine whether and to what extent the substance in question increased or decreased the rate of diffusion. These corrections have been applied to the coefficients for the non-electrolytes and curves are shown for both the uncorrected and corrected values.

Figure 1 shows the rates of diffusion for five substances in a 3.8% gelatin gel, Fig. 2 for nine substances in a 5% gel, the molecular weight range of the diffusate in each case being from 32 to 342.

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[1] An extract from a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Wisconsin.

[1a] Friedman and Kraemer, THIS JOURNAL, 52, 1295 (1930).

TABLE I

DIFFUSION OF VARIOUS NON-ELECTROLYTES IN A 3.8% GELATIN GEL

Diffusing substance	$\frac{1}{\sqrt{\text{Mol. wt.}}}$	Total time, hrs.	Expts.	Diffusion constants ($K \times 10^5$) Max.	Min.	Mean	Corrected
Methanol	0.177	216	8	0.866	0.442	0.626	0.710
Ethanol	.148	71	6	.660	.437	.576	.551
Glycerol	.104	71	6	.415	363	.390	.405
Mannitol	.074	214	8	.379	.296	.331	,331
Sucrose	.054	216	8	.264	.144	.209	.158

TABLE II

DIFFUSION OF VARIOUS NON-ELECTROLYTES INTO A 5% GELATIN GEL

Diffusing substance	$\frac{1}{\sqrt{\text{Mol. wt.}}}$	Total time, hrs.	Expts.	Diffusion constants ($K \times 10^5$) Max.	Min.	Mean	Corrected
Methanol	0.177	23	2	0.933	0.737	0.835	0.945
Ethanol	.148	70	2	.830	.817	.824	.790
Acetone	.131	121	3	.855	.427	.605	.589
Urea	.129	96	4	.668	.573	.618	.634
Trimethyleneglycol	.115	121	3	.765	.402	.528	.550
Pyridine	.113	121	3	.581	.410	.479	.470
Glycerol	.104	97	4	.351	324	.338	.351
Glucose	.075	96	4	.336	.188	.255	.240
Lactose	.054	67	2	.150	.138	.144	.141

It is to be noted that the points fall quite close to a straight line when the coefficient of diffusion is plotted against the inverse of the square root of the molecular weight, close enough to show that the size of the molecule does, to a large extent, determine the rate of diffusion, but each substance used does have its own specific influence upon the gelatin, altering its structure to change the rate of diffusion in the gel. The correction values determined in the next part of this paper do not place all of the values of the coefficients on the straight line, but do, in most cases, bring them much nearer to this relation. Even in studies of diffusion in water this relation does not hold much better, as shown by values given by Thovert[2] for the diffusion of

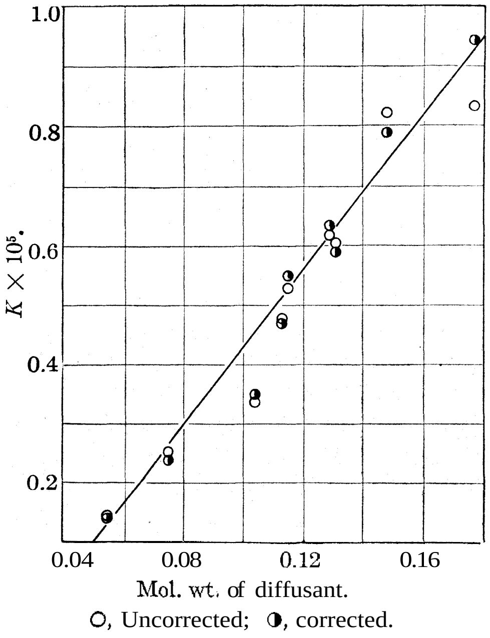

Fig. 2.—Diffusion of non-electrolytes in a gelatin gel.

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[2] Thovert, "Tabelles Annuelles Internationalles de Constantes," Vol. 4, p. 746.

about twenty non-electrolytes where his calculated values of $K\sqrt{M} \times 10^5$ varied from 5.9 to 8. This was, however, considered a satisfactory constant, and so it is felt that the relations shown for the diffusion in gels can be considered good indication that the diffusion laws hold in the gels.

TABLE III

EFFECT OF NON-ELECTROLYTES UPON DIFFUSION OF UREA INTO A 4.7% GELATIN GEL FROM A 3% SOLUTION

Substances present in the gel	Total time, hrs.	Expts.	Diffusion constants $(K \times 10^5)$ Max.	Min.	Mean	Increase in rate for urea, %
......	95	5	0.555	0 443	0 510	..
Urea	95	5	.546	.455	.497	– 2.5
Glycerol	97	5	.525	.432	.491	– 3.7
Glucose	99	5	.602	.512	.564	10.6
Ethanol	99	5	.615	.484	.532	4.3
......	47	7	.626	.567	.596	..
Sucrose	47	8	.932	.705	.791	32.7
Acetone	47	8	.731	.476	.608	2.8
Methanol	47	8	.555	.470	.525	– 11.9
......	53	7	.638	.592	.618	..
Lactose	52	9	.674	.576	.630	1.9
Ppidiie	51	8	.712	.510	.630	1.9
Trimethyleneglycol	52	9	.653	.557	.593	– 4.0

In order to determine the effect of various non-electrolytes on the diffusion process in gelatin gels, the gels were prepared to contain 1.5% of the non-electrolyte material and were then covered with a solution containing the same amount of the non-electrolyte (to avoid its diffusion) and in addition 3% of urea. The results are shown in Table III, where it is readily seen that most of the non-electrolytes have some effect upon the structure of the gels, the sucrose and glucose surprisingly large effects.

Effect of Temperature of Setting and Age of Gel upon Rate of Diffusion.—Because of the difficulty of reproducing results with gelatin gels with different previous heat treatment and the numerous references to the fact that the rate of setting determines to a large extent the physical structure of the gel, several investigations were made of the effect of temperature of setting and age upon the rate of diffusion in the gel. Gelatin gels cooled slowly are usually stronger physically, showing a more rigid solid structure. Hardy[3] has found that the more rapid the cooling the finer the structure will be. The results of the investigation are shown in Table IV.

From the (a) part it can be seen that if a gel is allowed to stand at one temperature long enough (in this case 92 hours), it will, for the most part, take up the structure of a gel originally set at that temperature. However, the other determinations show quite a variation in the diffusion constant.

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[3] Hardy, *J. Physiol.*, 24, 288 (1899).

TABLE IV

EFFECT OF TEMPERATURE OF SETTING AND AGE OF GEL UPON DIFFUSION OF UREA FROM A 3% SOLUTION INTO A GELATIN GEL MEASURED AT 5°

Temp. of setting, °C.	Kept at this temp., hours	Kept at 5°, hours	Total time, hours	Expts.	Diffusion constants ($K \times 10^5$) Max.	Min.	Mean
			(a) 4% Gel				
5	116	116	149	11	0.831	0.389	0.605
5	3	3	146	9	.695	.518	.597
0	24	92	143	10	.705	.443	.598
10	24	92	144	9	.711	.498	.603
24	24	92	145	9	.782	.390	.616
			(b) 5.2% Gel				
5	49	49	123	9	0.665	0.498	0.578
5	2	2	122	9	.586	.434	.514
0	50	0	123	8	.582	.457	.512
23	49	0	123	9	.545	.400	.481
23	24	25	125	8	.591	.492	.541
			(c) 4.3% Gel				
5	2	2	51	2	0.635	0.600	0.618
0	24	0	53	4	.613	.562	.589
23	27	0	54	4	.640	.419	.504

Since the information obtained from these experiments was so meager, diffusion at 5, 10, 15 and 20° was measured, using the same supply of gelatin and varying the conditions of setting as previously. The results are given in Table V, but not enough regularity has been shown here to warrant any quantitative discussion of the change in structure under these conditions.

TABLE V

EFFECT OF TEMPERATURE OF SETTING UPON DIFFUSION INTO A 5.1% GELATIN GEL

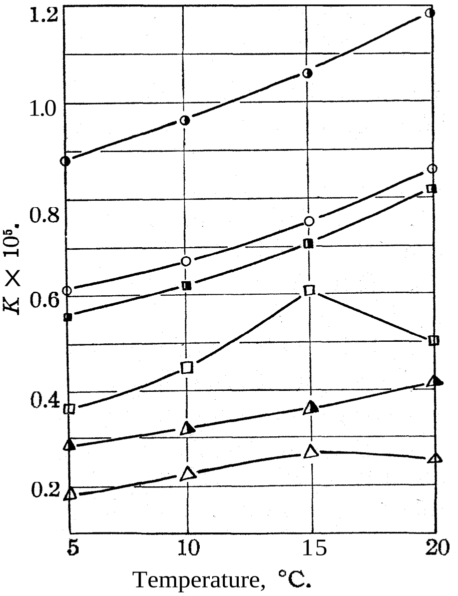
Temp. of setting, °C	Kept at this temp., hours	Temp. of diff., °C	Kept at this temp., hours	Total diff., hours	Expts.	Diffusion constants ($K \times 10^5$) Max.	Min.	Mean
			Urea from a 3% solution					
5	24	5	24	32	10	0.709	0.553	0.609
5	23	5	23	55	10	.609	.442	.535
25	24	5	1	31	9	.677	.541	.598
30	3	5	23	32	10	.846	.502	.593
0	24	5	2	33	9	.700	.545	.615
10	24	10	24	31	10	.751	.471	.667
24	24	10	1	32	11	.701	.477	.515
0	24	10	1	32	10	.757	.563	.693
15	24	15	24	29	10	.829	.605	.750
25	24	15	1	29	10	.820	.712	.772
0	24	15	1	29	10	.958	.710	.801
20	24	20	24	26	9	.990	.613	.859
25	24	20	1	25	9	.909	.644	.829
0	24	20	1	26	9	.855	.660	.767

TABLE V (*Concluded*)

Temp. of setting, °C.	Kept at this temp. houri	Temp. of diff., °C.	Kept at this temp., hours	Total diff., hours	Expts.	Diffusion constants ($K \times 10^5$) Max.	Min.	Mean
				Sucrose from a 3% solution				
10	24	10	24	33	11	0.274	0.187	0.220
15	24	15	24	29	10	.286	.228	.266
20	24	20	24	27	9	.297	.160	.252
				Glycerin from a 3% solution				
10	24	10	24	32	11	0.505	0.318	0.444
15	24	15	24	29	10	.706	.501	.606
20	24	20	24	27	9	.630	.350	.500

In Table VI the results of the last four runs are summarized and it is to be noticed that in three cases out of the four the gel set at 25° gives a lower rate of diffusion while that set at 0° gives a higher rate than the gel set at the temperature of diffusion. Qualitatively, then, the lower the temperature of setting the higher the rate of diffusion.

Figure 3 shows the rates of diffusion of urea, glycerol and sucrose in a 5.1% gelatin gel and in water at 5, 10, 15 and 20°; the variation is due to the change in structure at higher temperature causing slower diffusion. From each curve it is to be noted that at 20° there is much slower diffusion than would be expected from the values at 5°. The curve for glycerin in the gel shows a peculiar behavior, but roughly the same effect is noticeable. These curves would tend to substantiate the statement that gels set at lower temperature offer less resistance to diffusion than gels set at higher temperatures.



◑, Diffusion of urea in water; O, diffusion of urea in gel; A, diffusion of sucrose in water; A, diffusion of sucrose in gel; □, diffusion of glycerin in water; O, diffusion of glycerin in gel.

Fig. 3.—Diffusion in gels *vs.* temperature.

The values for the coefficients of diffusion in water at the various temperatures were obtained from the following values of $K \times 10^5$ given by Öholm:[4] sucrose, 0.380 at 22"; glycerin, 0.816 at 20°; and urea, 1.183 at 20°. To change to the various

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[4] Öholm, *Medd. Vetenskapsakad. Nobelinst.*, 2, n23.

TABLE VI

EFFECT OF TEMPERATURE OF SETTING UPON DIFFUSION OF UREA IN 5.1% GELATIN

Temp. of setting, °C.	$K \times 10^5$			
	5°C.	10°C.	15°C.	20°C.
25	0.598	0.565	0.772	0.829
0	.615	.693	.801	.767
Temp. of diff.	.609	.667	.750	.859

TABLE VII

DIFFUSION IN 5.1% GELATIN GELS AT DIFFERENT TEMPERATURES

Diffusing substance	$K \times 10^5$			
	5°C.	10°C.	15°C.	20°C.
Urea	0.609	0.667	0.750	0.859
Glycerin	.363	.444	.606	.500
Sucrose	.182	.220	.266	.252

DIFFUSION IN WATER AT DIFFERENT TEMPERATURES CALCULATED FROM ÖHOLM

Diffusing substance	$K \times 10^5$			
	5°C.	10°C.	15°C.	20°C.
Urea	0.880	0.962	1.061	1.183
Glycerin	.552	.618	0.704	0.816
Sucrose	.285	.318	.359	.413

temperatures, use was made of the empirical equation $K_{t_1} = K_{t_2}/1 + \alpha(t_2 - t_1)$, where a = $0.026 - 0.021 \log K$.[5]

Summary

1. Diffusion constants for several non-electrolytes in gelatin gels have been determined.

2. It has been shown that the diffusion laws hold for these compounds in gelatin gels.

3. It has been found that each non-electrolyte has a very specific action on the rate of diffusion in gelatin gels; those outstanding were the increase by sucrose of 32%, and the decrease by methanol of 12%.

4. Study of the effect of temperature of setting and age of the gel has shown that, in general, gels set at low temperature are more permeable to molecules than those set at higher temperature. This has been interpreted to indicate a more open structure.

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[5] Öholm, *Z. physik. Chem.*, 70,399 (1909).

[CONTRIBUTION FROM THE COLLOID LABORATORY, UNIVERSITY OF WISCONSIN]

STRUCTURE OF AGAR GELS FROM STUDIES OF DIFFUSION[1]

BY LEO FRIEDMAN

RECEIVED JUNE 10, 1929 PUBLISHED APRIL 7, 1930

Although agar forms a gel very readily and is quite easily handled, the investigations of diffusion in gels seem, for the most part, to have been carried out in gelatin systems. Voigtlander[1a] studied the diffusion of four electrolytes in agar gels at 20° and came to the conclusion that the diffusion constant is independent of the concentration of gel. Bechhold and Ziegler[2] paralleled their studies in gelatin with some in agar, finding a 15% decrease in the rate of diffusion of the juice of red beet as the concentration of agar was increased from 1 to 4%. Fricke,[3] while developing his micro-slicing method, made a few determinations of the diffusion of sodium chloride in agar, but no extensive studies were made of the properties of the agar systems.

Experimental

The agar used in these studies was the ordinary commercial material carefully purified by preliminary soaking in acetic acid and water, followed by electrodialysis. This purification process, however, removing most of the electrolytes also destroyed some of the gelling properties of the agar, for as the iso-electric point is approached the gel becomes less stable.

The procedure followed in the determination and calculation of the diffusion constants was the same as that used in the studies on gelatin.[4] Because of the fact that agar does not stick to glass it was necessary to line the bottles with a Bakelite varnish which adhered closely to the glass and to which the agar would stick.

Effect of Concentration of Gel on Rate of Diffusion.—To show the effect of concentration of agar upon the structure of the gels, determinations of the rates of diffusion of urea and glycerin were made in various concentrations of purified gels. Curve a, Fig. 1, shows the diffusion of urea in agar gels. Between the concentrations of 0.8 and 5.15% the diffusion is slowed down 36%, in contradiction to the work of Voigtlander. Curve b, Fig. 1, shows the diffusion of glycerin in agar gels.

Dimensions of the Gel Framework in Agar Gels.—Using the same equations and methods as in the calculations for gelatin,[4] the size of the openings in the solid framework of agar gels has been calculated from the curves in Fig. 1. The results of these calculations are shown in Table II. The larger values for the radii from the glycerin determinations would be

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[1] An extract from a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Wisconsin.

[1a] Voigtlander, *Z. physik. Chem.*, 3, 316 (1889).

[2] Rechhold and Ziegler, *ibid.*, 56, 105 (1906)

[3] Fricke, *Z. Elektrochem.*, 31, 430 (1926)

[4] Friedman and Kraemer, THIS JOURNAL, 52, 1295 (1930).

TABLE I

DIFFUSION IN AGAR GELS VS. CONCENTRATION OF GEL

Agar concn., %	Total diff., hours	Expts.	Diffusion constants ($K \times 10^5$) Max.	Min.	Mean
	(a)	Urea into the gel from a 3% solution			
0.79	46	8	0.777	0.690	0.740
1.05	51	10	.797	.617	.727
1.11	18	3	.757	.707	.739
1.50	49	11	.845	.544	.694
1.58	48	10	.777	.570	.691
1.64	18	3	.736	.695	.710
2.39	49	8	.622	.554	.582
3.16	17	3	.670	.530	.591
3.16	48	10	.662	.465	.590
4.08	49	9	.609	.461	.518
5.15	48	10	.500	.442	.472
	(b)	Glycerin into agar from a 3% solution			
2.06	33	8	0.322	0.281	0.297
3.01	33	10	.426	.123	.272
3.91	33	10	.295	.192	.244
6.02	33	10	.245	.138	.199

expected from the tremendous effect which glycerin has on the agar. In the latter part of this paper it is to be noted that glycerin increased the rate of diffusion of urea in agar by 50%, which means that it had modified the structure to allow this faster diffusion.

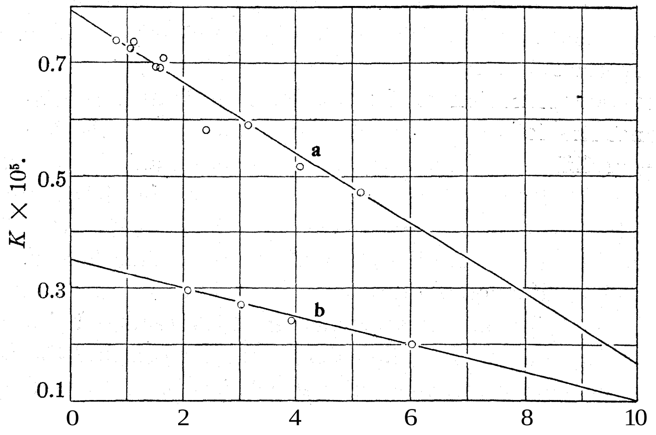

Fig. 1.—Diffusion in agar gels.

The order of magnitude of the radii of the pores in the agar gels is the same as that found for gelatin gels. However, the pores are decidedly smaller in the agar gels, as would be expected from the fact that a 1% agar gel is about as strong physically as a 5% gelatin gel.

TABLE II

SIZE OF THE PORES IN AN AGAR GEL

Substance diffusing		Urea	Glycerin
Radius of pores	2% gel	2.9mμ	5.65mμ
	5% gel	0.74mμ	1.43mμ

Diffusion of Non-Electrolytes in Agar.—It was found in the work on gelatin gels[4] that the rate of diffusion of a non-electrolyte was determined to a large extent by the molecular weight or size of the diffusing molecule, although it also was influenced by the specific effect of that non-electrolyte on the gelatin. Similar studies have been carried out with agar gels.

TABLE III

DIFFUSION OF VARIOUS NON-ELECTROLYTES IN AGAR GELS

Diffusing substance	$\frac{1}{\sqrt{\text{Mol. wt.}}}$	Total diff., hours	Expts.	Diffusion constants ($K \times 10^5$) Max.	Min.	Mean
(a) Diffusion into 0.79% gel from 3% solutions						
Urea	0.129	50	10	0.693	0.546	0.629
Trimethylene glycol	.115	48	8	.470	.392	.439
Dextrose	.075	50	10	.369	.292	.327
Sucrose	.054	50	11	.306	.197	.247
(b) Diffusion into 5.15% gels from 3% solutions						
Ethyl alcohol	0.148	47	9	0.527	0.282	0.393
Urea	.129	48	10	.500	.442	.472
Propyl alcohol	.129	48	10	.563	.244	.330
Pyridine	.113	48	10	.362	.202	.316

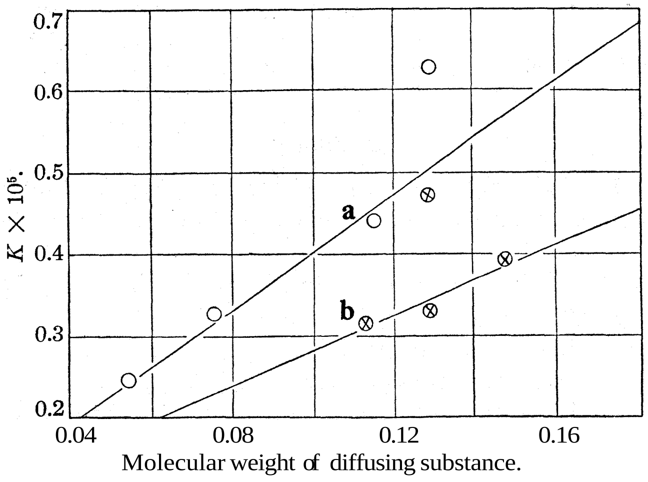

Fig. 2.

Curve a, Fig. **2,** shows the diffusion of four non-electrolytes in 0.8% agar gels. Corrected values were not calculated,[4] because the agar used for these studies was electrodialyzed to a different extent than that used for the studies of the effect of the non-electrolytes discussed later. Curve b, **Fig.** 2, shows the diffusion of four non-electrolytes in a 5.15% agar gel. The relation that $K^2 \times M$ = a constant is indicated but the variation is quite large. The specific action of the non-electrolyte upon the agar is too great to permit drawing any more quantitative conclusions.

Effect of Non-Electrolytes on Rate of Diffusion.—To determine the effect of various non-electrolytes on the diffusion process in agar gels, experiments similar to those performed with gelatin were carried out.[4] It was found that ethyl alcohol alone, of those non-electrolytes used, decreased the rate of diffusion of urea in agar, whereas glycerin, dextrose and trimethyleneglycol caused enormous increases, as shown in Table IV.

TABLE IV

EFFECT OF NON-ELECTROLYTES UPON DIFFUSION OF UREA INTO AGAR GELS FROM A 3% SOLUTION

Substance present in the gel	Total diff., hours	Expts.	Diffusion constants ($K \times 10^5$) Max.	Min.	Mean	Increase in rate for urea, %
			Diffusion into 1.5% gels			
......	49	11	0.845	0.544	0.694	..
Ethyl alcohol	48	10	.796	.420	.646	– 6.9
Glycerin	48	11	1.100	.891	1.036	49.3
Lactose	48	10	0.827	.583	0.739	6.5
Sucrose	48	11	.825	.503	.714	2.9
			Diffusion into 3% gels			
......	45	11	0.524	0.418	0.470	..
Methyl alcohol	46	10	.585	.405	.531	13.0
Urea	26	6	.603	.375	.518	10.2
Trimethyleneglycol	46	10	.928	.597	.697	48.2
Dextrose	46	10	.975	.714	.809	72.0

Summary

1. A study of the diffusion of non-electrolytes in gels of agar has been made; diffusion coefficients for several non-electrolytes have been determined.
2. It has been shown that the rate of diffusion in agar gels decreases linearly as the concentration of gel increases.
3. The possible dimensions of the gel framework have been calculated from the rates of diffusion of non-electrolytes in the gels.
4. The relation between the molecular weight of the diffusate and its rate of diffusion in the gel has been shown to be the same as in a liquid medium.
5. The effect of various non-electrolytes upon the structure of the gel framework has been investigated through their influence on the rate of diffusion of *a* single diffusate.

UNIVERSITY OF OREGON, EUGENE, OREGON

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE ROYAL AGRICULTURAL COLLEGE, COPENHAGEN]

A STUDY OF CELLS WITH LIQUID–LIQUID JUNCTIONS

BY E. A. GUGGENHEIM

RECEIVED JUNE 17, 1929 PUBLISHED APRIL 7, 1930

The object of this research was to investigate both theoretically and experimentally the electromotive force of cells with liquid–liquid junctions, especially the effect of the nature of the junction on the value, stability and reproducibility of the measured electromotive force, and finally to show that both stability and reproducibility are experimentally realizable under just the conditions to be expected from theoretical considerations.

Theoretical Considerations.—As we are primarily interested in the conditions for the stability and reproducibility of the cells rather than with the absolute values of the e. m. f., we shall here make the simplifying and inaccurate assumption that the ions obey the laws of ideal dilute solutions. Any deviations from the truth of this assumption will be referred to as "salt effects"; these may greatly affect the absolute values of the e. m. f., but not its reproducibility nor to any great extent its stability; a discussion of "salt effects" will be given elsewhere.[1] It will also be sufficient for all the points which we wish to emphasize if we consider solutions containing only univalent ions; the more general case of solutions containing ions of different valency makes the formulas somewhat more involved without introducing any new physical complications.

Let c_i denote the concentration, μ_i the chemical potential, z_i the valency, taking account of its sign, u_i the mobility and t_i the transport number of ions of type i. It is then a well-known thermodynamic result that the liquid–liquid junction potential $d\phi$ due to diffusion between a solution with concentrations c_i and another with slightly different concentrations $c_i + dc_i$ is given by the formula

$$-\epsilon d\phi = \Sigma_i z_i t_i \, d\mu_i \qquad (1)$$

where $-\epsilon$ is the charge of an electron and z_i is $+1$ or -1 according as the ion i is positively or negatively charged. The assumption that the ions obey the laws of ideal dilute solutions implies the relation

$$\mu_i = RT \log_e c_i + \mu_i^0 \qquad (2)$$

where R is the gas constant, T the absolute temperature and μ_i° depends on the temperature and the solvent but not the concentration. Substituting (2) in (1) we get

$$-\epsilon d\phi = RT\, \Sigma_i z_i t_i \frac{dc_i}{\quad} \qquad (3)$$

but by the definition of transport number

$$t_i = \frac{u_i c_i}{\Sigma_j u_j c_j} \qquad (4)$$

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[1] Guggenheim, *J. Phys. Chem.*, **36**, in press.

whence

$$-\epsilon d\phi = RT \frac{\Sigma_i z_i u_i \, dc_i}{\Sigma_i u_i c_i} \tag{5}$$

Since the transport of ions on the passage of current from a solution of concentrations c_i to another with concentrations $c_i + dc_i$ is reversible, the applicability of thermodynamics to the problem can hardly be questioned, and Equation 5 may safely be regarded as strictly valid for univalent ions obeying the laws of ideal dilute solutions. If however there are finite differences between the concentrations of the two solutions in contact, the transfer of at least some of the ions on the passage of current may be irreversible; for example, if the first solution contains a finite quantity of ions of a type not present at all in the second solution, then the passage of a minute current in the one direction will carry some ions of this type into the second solution, but a reversal of the current will not return them. To apply thermodynamics to junctions with finite differences in the concentration we have to assume a transition layer of intermediate composition varying continuously from that of the first solution at the one end to that of the second at the other. If at any time we know the concentrations at all points of the transition layer we can obtain the whole liquid–liquid junction potential ϕ by integration of *(5)*

$$-\epsilon\phi = RT \int_{I}^{II} \frac{\Sigma_i z_i u_i \, dc_i}{\Sigma_i u_i c_i} \tag{6}$$

where I denotes the first solution and II the second. In the simple case of a concentration cell where Solutions I and II contain only one uni-univalent salt, the same in both, the integrand in *(6)* is a perfect differential and so the integral can be evaluated directly. Using the suffixes + and − to refer to the cations and anions respectively, setting

$$c_+ = c_- = c \qquad z_+ = +1 \qquad z_- = -1 \tag{7}$$

and regarding the mobilities as independent of the concentrations, we get

$$-\epsilon\phi = RT \frac{u_+ - u_-}{u_+ + u_-} \log_e \frac{c^{II}}{c^{I}} \tag{8}$$

But in the general case of more than two species of ions the integrand in (6) is not a perfect differential and so the integration cannot be performed without further knowledge of the variation of the concentrations along the transition layer. In other words, in the case of more than two ionic species the junction potential will depend on the nature of the junction.

The type of junction most easily treated mathematically is that which we will call the "continuous mixture layer." Its nature is defined as follows: the composition at any point of the transition layer is a linear combination of the compositions of the extreme liquids I and II; or, in other words, the solution at any point of the transition layer may be regarded as a mixture in certain proportions of the two extreme solutions, I and II. For these conditions (6) can be integrated directly if one treats the mobilities as independent of the concentrations. The result is

$$-\epsilon\phi = KT\,\frac{\Sigma_i z_i u_i (c_i^{II} - c_i^{I})}{\Sigma_i u_i (c_i^{II} - c_i^{I})}\log_e \frac{\Sigma_i u_i c_i^{II}}{\Sigma_i u_i c_i^{I}} \tag{9}$$

a formula which we owe to Henderson,[1a] but neither his experiments nor those of subsequent writers were designed in such a way as to fulfil the conditions corresponding to the assumptions underlying this particular integrated form of the general differential equation, (6). Experiments to be described below show that when these conditions are observed, reproducible values are obtained for the e. m. f. measured. In the particular case where the solutions I and II have equal specific conductivities

$$\Sigma_i u_i c_i^{I} = \Sigma_i u_i c_i^{II} = S \tag{9a}$$

and Equation 9 becomes indeterminate. In this case we have

$$-\epsilon\phi = RT\int_0 \frac{\Sigma_i z_i u_i (c_i^{II} - c_i^{I})\mathrm{d}\lambda}{S} = RT\,\frac{\Sigma_i z_i u_i (c_i^{II} - c_i^{I})}{S} \tag{9b}$$

A second type of junction which allows (6) to be integrated explicitly is what we shall call the "constrained diffusion junction." It may be described as follows: the composition of the liquid is artificially maintained constant and the same as that of Solution I at all points to the left of a certain fixed plane A; similarly, the composition to the right of another parallel plane B is maintained the same as that of Solution II; subject to these constraints the ions diffuse freely between A and B until a steady state is reached, after which the junction potential should remain constant. The solution corresponding to these contraints shows that the difference of potential ϕ between A and B is independent of the distance A B and is determined by the transcendental equation

$$\frac{\Sigma_+ u_i c_i^{II}\, e^{\epsilon\phi/RT} - \Sigma_+ u_i c_i^{I}}{\Sigma_- u_i c_i^{II} - \Sigma_- u_i c_i^{I}\, e^{\epsilon\phi/RT}} = \frac{\log_e \dfrac{\Sigma_i c_i^{II}}{\Sigma_i c_i^{I}} - \dfrac{\epsilon\phi}{RT}}{\log_e \dfrac{\Sigma_i c_i^{II}}{\Sigma_i c_i^{I}} + \dfrac{\epsilon\phi}{RT}} \times \frac{\Sigma_i c_i^{II}\, e^{\epsilon\phi/RT} - \Sigma_i c_i^{I}}{\Sigma_i c_i^{II} - \Sigma_i c_i^{I}\, e^{\epsilon\phi/RT}} \tag{10}$$

where Σ_i, Σ_+, Σ_-, denote, respectively, summation over all ions, over all positive ions and over all negative ions. This formula for solutions containing only ions of the same numerical valency was given by Planck.[2] The corresponding more general formula for ions of several different valencies was obtained by Pleijel.[3]

As was only to be expected this solution is in general different from that of Henderson, because under the conditions of constrained diffusion a steady state is reached in which the solution at each point cannot be

[1a] Henderson, *Z. physik. Chem.*, 59, 118 (1907); **63**, 325 (1908).

[2] Planck, *Wied. Ann.*, **39**, 161 (1890); 40, 561 (1890).

[3] Pleijel, *Z. physik. Chem.*, 72, 1 (1910).

regarded as a mixture of the two extreme liquids. The values given by the formulas of Henderson and of Planck for various junctions have been compared by Cumming and Gilchrist.[4] For the junction hydrochloric acid of concentration c (Solution I) against potassium chloride of concentration kc (Solution 11), the difference is zero when $k = 1$. For $k < 1$ the continuous mixture layer gives the higher potential difference while the opposite is the case when $k > 1$. As long as the concentration of the potassium chloride is greater than that of the hydrochloric acid, the difference between the potentials given by the two formulas is never more than 1.5 millivolts; the difference is maximum in the neighborhood of $k = 5$. Both formulas give a flat minimum in the neighborhood of $k = 10^3$. The position of the minimum depends very much on the exact value assumed for the transport numbers of K^+ and Cl^- in potassium chloride.

The physical conditions corresponding to the Planck formula have not generally been understood.[5] There is no restriction as to the "sharpness" of the boundary, the potential being in fact independent of the length of the transition layer provided there is a steady state in which the length of the layer is artificially maintained constant. It was suggested by Bjerrum[6] that these conditions might be obtained if the junction were within a membrane kept washed on the two sides with the two outer solutions, but apparently this has never been tried previous to the author's attempts to be described in a later section. The only other evidence the author has been able to find of Planck's formula being correctly interpreted is in an unpublished fragment of Gibbs.[1]

A third definite type of junction is that which may be described as the "free diffusion junction"; the conditions defining it are that the transition layer should be initially short compared with the distance between the two electrodes, an absolutely sharp boundary being of course impossible, and that unconstrained diffusion should be allowed to take place. Under these conditions the length of the transition layer is always increasing, but, if there is cylindrical symmetry, that is, if the gradients of the concentrations and of the electrical potential are throughout parallel to a fixed straight line, it appears that the potential difference between the ends is independent of the time, at least after a sufficient time has elapsed for the effect of the initial deviations from "sharpness" to have died out. This type of junction has been discussed by Taylor.[8] The fundamental equations cannot be integrated explicitly with these boundary conditions.

[4] Cumming and Gilchrist, *Proc. Faraday Soc.*, 9, 174 (1913).

[5] Cumming and Gilchrist, *ibid.*, 9, 174 (1913); Biichi, *Z. Elektrochem*, 30, 443 (1924); Planck, *Sitzb. Preuss. Acad. Wiss.*, 34, 285 (1927).

[6] Bjerrum, *Z. Elektrochem.*, 17, 58 (1911).

[7] Gibbs, "Collected Works," Vol. I, p. 431.

[8] Taylor, *J. Phys. Chem.*, 31, 1478 (1927).

Taylor has therefore tried to obtain an approximate solution.[9] In order to follow Taylor it is best to consider first the free diffusion of a non-electrolyte obeying the laws of ideal dilute solutions. We shall suppose that there is cylindrical symmetry, all gradients being parallel to the x-axis. Let c denote the concentration and μ the chemical potential of the solute; let u denote the mobility of a solute molecule and V its velocity; let t be the time, T the absolute temperature and R the gas constant. Then the equation of continuity is

$$\frac{\partial c}{\partial t} = -\frac{\partial}{\partial x}(cV) \tag{11}$$

and the equation of motion

$$V = -u\frac{\partial \mu}{\partial x} = -u\frac{RT}{c}\frac{\partial c}{\partial x} \tag{12}$$

Substituting from (11) into (12) we obtain the general differential equation for the diffusion of an ideal solute

$$\frac{\partial c}{\partial t} = RTu\frac{\partial^2 c}{\partial x^2} = \kappa\frac{\partial^2 c}{\partial x^2} \tag{13}$$

where $\kappa = RTu$ is the "diffusion coefficient."

For the case of "free diffusion" between two solutions of concentrations c_0 + A and c_0 − A, the boundary conditions are

For all t $c = c_0 + \Delta$ for $x = +\infty$ $c = c_0 - \Delta$ for $x = -\infty$
For $t = 0$ $c = c_0 + \Delta + f(x)$ for $x > 0$ $c = c_0 - \Delta + f(x)$ **for $x < 0$**

where $f(x) = 0$ except for $-l < x < +l$ in which interval $f(x)$ is indefinite and may even be discontinuous provided it remains finite. f(x) is a measure of the uncontrollable initial deviations from "sharpness." The exact solution of (13) is

$$c = c_0 + \Delta\frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{\kappa t}}} e^{-\xi^2}\,d\xi + \frac{1}{2\sqrt{\pi\kappa t}}\int_{-l}^{+l} f(\xi)\,e^{-(\xi - x)^2/4\kappa t}\,d\xi \tag{14}$$

From the form of the last term it may be shown that the influence of the initial deviations from sharpness will be halved in a time not greater than l^2/κ and will have completely died out when t is several times as great as l^2/κ. After this initial period, c is a function of $x/\sqrt{t}$; hence if at any time, t_1, we plot c against x, this same curve will also represent c as a function of x for any subsequent time t_2 provided only we alter the scale of x in the ratio $\sqrt{t_2/t_1}$. This solution should give a general idea of the nature of the solution for the corresponding case of electrolytes, which we shall consider next.

For ions of type i we have the equation of motion

$$V_i = u_i\left[-\frac{\partial \mu_i}{\partial x} - z_i\epsilon\frac{\partial \psi}{\partial x}\right] \tag{15}$$

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[9] Since the present paper was first submitted for publication in June, 1929, the author has been in correspondence with Dr. Taylor and his criticism of Dr. Taylor's treatment is modified in consequence.

where ψ is the electric potential at the plane x, so that in place of (21) we get the general differential equation for ionic diffusion

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x}\left[u_i c_i \frac{\partial \mu_i}{\partial x} + u_i c_i z_i \epsilon \frac{\partial \psi}{\partial x}\right] \qquad (16)$$

If we multiply by z_i, sum over all i and use the condition of electrical neutrality

$$\Sigma_i z_i c_i = 0 \qquad (17)$$

we get

$$-\epsilon \frac{\partial \psi}{\partial x} = \frac{\Sigma_i z_i u_i c_i \frac{\partial \mu_i}{\partial x}}{\Sigma_i u_i c_i} = RT \frac{\Sigma_i z_i u_i \frac{\partial c_i}{\partial x}}{\Sigma_i u_i c_i} \qquad (18)$$

This equation derived from dynamic considerations is equivalent to (5), which was obtained thermodynamically. Substituting from (18) into (16)

$$\frac{\partial c_i}{\partial t} = RTu_i \frac{\partial^2 c_i}{\partial x^2} - \frac{\partial}{\partial x}\left[u_i c_i z_i\, RT \frac{\Sigma_j z_j u_j \frac{\partial c_j}{\partial x}}{\Sigma_j u_j c_j}\right] \qquad (19)$$

There are as many equations of this form as there are types of ions.

For the case of "free diffusion" the boundary conditions are

for all t $c_i = c_i^\circ + \Delta_i$ for $x = +\infty$ $c_i = c_i^\circ - \Delta_i$ *for* $x = -\infty$
where $2c_i^\circ = c_i^{I} + c_i^{II}$ and $2\Delta_i = c_i^{II} - c_i^{I}$

There are also the boundary conditions for $t = 0$, but the effect of these, as in the case of a non-electrolyte, will fall to one-half in a time of the order l^2/RTu_i, where l is the length of the initial transition layer whose nature will be accidental and irreproducible; when the time is great compared with l^2/RTu_i the effect of the initial deviations from sharpness will be negligible. The diffusion coefficient $\kappa_i = RTu_i$ is for univalent ions generally of the order 1 cm.^{2}/day, so that if the initial irregular transition layer has a length 0.5 mm., its effect will be halved in about four minutes and will be negligible in thirty to forty minutes. After this transient period the solution will be the same as if the initial boundary had been infinitely sharp; but from the form of Equation 19 and the boundary conditions it is clear that the solution must take the form that c_i is a function of x, t the various c_j°, Δ_j and the various $\kappa_j = RTu_j$, but all the c_j°, Δ_j have the same dimensions as c_i, while the κ_j have the same dimensions as x^2/t; therefore, the solution will, as in the case of a non-electrolyte, be of such form that c_i is a function of x^2/t or of $y = x/2\sqrt{t}$. Taylor comes to this conclusion by a similar argument. His reasoning is, however, somewhat obscured chiefly by a misprint of t/x^2 instead of x^2/t and to a less extent by his appearing to ignore the dimensions of energy which cancel out owing to the peculiar units used by him. We thus have

$$\frac{\partial^2 c_i}{\partial x^2} = \frac{d^2 c_i}{dy^2} \times \frac{1}{4t} \qquad \frac{\partial c_i}{\partial t} = -\frac{dc_i}{dy} \times \frac{y}{2t} \qquad (20)$$

Substitution in (26) gives

$$-2y\frac{\mathrm{d}c_i}{\mathrm{d}y} = \kappa_i\frac{\mathrm{d}^2c_i}{\mathrm{d}y^2} - \frac{\mathrm{d}}{\mathrm{d}y}\left[\kappa_i c_i z_i\,\frac{\Sigma_+\kappa_j\dfrac{\mathrm{d}c_j}{\mathrm{d}y} - \Sigma_-\kappa_j\dfrac{\mathrm{d}c_j}{\mathrm{d}y}}{\Sigma_j\kappa_j c_j}\right] \tag{21}$$

where we have written the diffusion coefficient κ_i in place of RTu_i. If all the ions had the same mobility and so the same diffusion coefficient κ, (21) would reduce to

$$-2y\frac{\partial c_i}{\partial y} = \kappa\frac{\partial^2 c_i}{\partial y^2} \tag{22}$$

with the solution

$$c_i = c_i(y) = c_i^\circ + \Delta_i\frac{2}{\sqrt{\pi}}\int_0^{y/\sqrt{\kappa}} e^{-\xi^2}\,\mathrm{d}\xi \tag{23}$$

equivalent to (14) without the transient term. Taylor next asserts that when the mobilities are not all equal, the solution of (21) can take the form

$$c_i = c_i(y) = N_i + \sum_{n=0}^{\infty} A_n^i\int_0^{y/\sqrt{\gamma_i}} e^{-\xi^2}\,\xi^n\,\mathrm{d}\xi \tag{24}$$

where the N_i, A_n^i and γ_i are constants. Actually it can be shown that any continuous monotonic function of y which tends to a finite limit when y tends to $+\infty$ or $-\infty$ can be expressed in the form of the right-hand side of (24); moreover, the value of γ_i in such an expansion is quite arbitrary. Whether the form given by (24) is of any value depends therefore on whether the series converges rapidly, and this will depend on the value chosen for γ_i. The convergence would generally be very slow if one simply set $\gamma_i = \kappa_i$. If one could find a particular value of γ_i to make the series in (24) converge rapidly for all values of y, it might possibly be sufficient to retain only the first term of the series; (24) would then take the form (23) with γ_i in the place of κ_i. Taylor indeed suggests this form as an approximate solution and shows how to choose γ_i so as to give the most rapid possible convergence of the series and so the best possible fit for small values of y. With such a value of γ_i a slowly convergent series may be required to give a reasonably good fit over the whole range of y and the first term might well give a bad fit for larger values of y. In Taylor's opinion this can never be so bad as to more than counteract the exact fit at $y = 0$ and $y = *\infty$. This he has, however, not proved and is in the author's opinion a rather dangerous assumption, especially in cases where the diffusion potential given by the "free diffusion junction" differs widely from that of the "continuous mixture layer." In junctions of the type concentrated acid against dilute neutral salt this may well be the case, but such junctions are rarely used in practice. Taylor actually applies his computation only to the case of hydrochloric acid against potassium chloride of the same concentration, where the difference between the two types of junction is only 0.3 to 0.4 mv. Taylor points out a check on his approximation by comparison of the computed cation and anion concentrations at various planes in the transition layer. Theoretically these should, of course, be equal. Even if they were found so in his check this would not be sufficient proof that his approximation gave the true distribution. Actually one finds that at those parts of the transition layer where the fit is not automatically good, the differences between the computed cation and anion concentrations differ by from 37 to 56% of the deviation of composition from that of a mixture of the electrode solutions. It is difficult to estimate the inaccuracy of the approximation, but in view of the above figures the present author thinks it may be a not inappreciable fraction of the correction term to the "continuous mixture" value. It is easy to show that for a single uni-univalent salt the diffusion equation can be integrated exactly, the solution being of precisely the same form as for a non-electrolyte, the effective diffusion coefficient being the harmonic mean of those of the two ions, that is to say that we have to set in Equation 14

$$\frac{1}{\kappa} = \frac{1}{2}\left(\frac{1}{\kappa_+} + \frac{1}{\kappa_-}\right) \qquad (25)$$

The author, therefore, suggests as an approximate solution of the diffusion equation for several electrolytes with a common anion that each salt (but not each ion) be assumed to diffuse independently of the others. This solution, in contrast to Taylor's, will at least satisfy the condition of electrical neutrality and has, moreover, the advantage of considerably greater simplicity. Which solution will in a given case be the more accurate it is difficult to judge. For the particular junction considered by Taylor the difference between the two solutions is inappreciable. It is most unfortunate that the mathematical treatment of the "free diffusion junction" should be so intractable, even when all salt effects are neglected, the more so as experiment shows that of the three junctions discussed it is the simplest to produce, the most stable and quite as reproducible as the better of the other two discussed above.

A fourth type of junction must also be discussed briefly, not because of its simple nature, but because, unlike the other three types so far discussed, it corresponds exactly to conditions that have been used in practice; the type of junction referred to is that known as the "flowing junction." In this junction the two solutions stream toward each other and after meeting flow away in parallel streams. The characteristic feature of this type of junction is the extreme thinness of the transition layer. The flowing junction was used first by Lamb and Larson[10] and shortly after by MacInnes and Yeh.[11] In both cases excellent reproducibility is reported. The former authors do not discuss theoretically the nature of the transi-

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[10] Lamb and Larson, THIS JOURNAL, 42, 229 (1920).

[11] MacInnes and Yeh, *ibid.*, **43**, 2563 (1921).

tion layer; the latter believe it to be the same as that which we have discussed above under the name "continuous mixture layer." This assumption seems surprising because the thinner the layer the greater is the importance of diffusion as compared with mixing, but this particular type of junction is characterized by the thinness of the transition layer. An alternative possibility is that it rather resembles the junction described above under the name "constrained diffusion" except for the complete absence of cylindrical symmetry. There will certainly be a steady state which will depend very little on the rate of flow provided it is sufficiently great and yet not so great as to produce turbulence; on the other hand, it may well depend on the curvature of the stream lines and so on the exact shape of the apparatus used. There is also the possibility that neither mixing nor diffusion can be neglected, although in this case one would expect changing the rate of flow to have a detectable effect,, which has not been observed. Scatchard,[12] who has also used the flowing junction with success, writes[13] "I have always regarded our flowing junctions as 'continuous mixture boundaries' because it seems to me that the time is too short for diffusion to become noticeable but I know no way of demonstrating their nature." It should be possible to check this if one knew the thickness of the transition layer, the rate of flow and the diffusion coefficients. Although the "flowing junction" has in certain cases given greater reproducibility than any other type of junction previously tried, its interest from a theoretical point of view must be considerably diminished by the uncertainty of the factors which determine the steady state. If the steady state observed is independent of the shape of the apparatus, it seems likely that the junction must *"a posteriori"* be of the "continuous mixture" type. If, on the other hand, the steady state observed depends on the curvature of the stream lines, its theoretical consideration will be too complicated to be worth attempting.

Previous Measurements of Cells with Liquid-Liquid Junctions.—The numerous researches involving the use of cells with liquid–liquid junctions fall into two classes: those in which the junction potential was made as small as possible (usually by making one of the two liquids a concentrated solution of potassium chloride) and neglected, and those in which the junction potential was appreciable and was one of the factors of primary interest. We need discuss previous work of the latter class only. Almost all investigators mention that the e. m. f. observed is not constant, but may change several millivolts through "aging"; such effects are reported for example by Weyl,[14] and by Lewis and Rupert.[15]

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[12] Scatchard, THIS JOURNAL, 47, 696 (1925).

[13] Private communication to the author.

[14] Weyl, "Dissertation," Karlsruhe, 1905.

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

This is explained by Bjerrum[16] on the assumption that there is initially a transition layer of the "continuous mixture" type, which owing to its thinness is unstable and is soon disturbed by diffusion effects. Chanos[17] found that a symmetrical cell with two liquid–liquid junctions could give e. m. f. values up to 6 mv. if one of the junctions was stirred. Cumming and Gilchrist[18] also report one cell in which the e. m. f. rose 11 mv. in the first ten minutes and a further 10 mv. in twenty-four hours; they also report an e. m. f. as high as 15 mv. in a cell symmetrical except as regards the age of the two junctions. These authors made an extended study of the reproducibility and stability of junctions formed in various ways, but their discussion shows a lack of understanding of the essential characteristics of a junction that determines its reproducibility. For example, they associate the Planck formula with a "sharp" boundary; actually the initial transition layer is almost certainly formed by mixing and the most immediate consequence of "sharpness" is instability. They also associate the Henderson formula with a transition layer in which the two extreme solutions A and B have been mechanically mixed by stirring; this procedure merely transforms the indefinite type of junction between A and B into two junctions of equally indefinite type, one between A and C, the other between C and B, where C denotes the solution obtained by stirring A and B together.

In certain cases fair reproducibility in the initial values of the e. m. f. has been obtained, as for example by Lewis and Sargent[19] and by Lewis, Brighton and Sebastian,[20] but in every case the liquid–liquid junctions were between two solutions of the same concentration of two uni-univalent salts with one ion in common. All the measurements by the flowing junction method of Lamb and Larson[10] and those of MacInnes and Yeh[11] were also on cells of this type, From this brief review of the literature there appears no evidence of reproducibility and stability ever having been obtained in a cell containing a junction between two solutions of different electrolytes at different concentrations, unless one of these was a concentrated solution of potassium chloride.

Experimental Technique

All the cells measured were of the type

$$\mathrm{Hg} \mid \mathrm{HgCl} \mid 0.1\ N\ \mathrm{HCl} \mid c\ \mathrm{KCl} \mid 0.1\ N\ \mathrm{KCl} \mid \mathrm{HgCl} \mid \mathrm{Hg}$$

where the concentration c of the potassium chloride bridge was varied from 0.1 to **3.5** N. In choosing this type of cell there were several points considered to be in its favor. First, the *e.* m. f. measured is due entirely

[16] Bjerrum, *Z. Elektrochem.,* 17, *58* (1911).

[17] Chanos, *Ann. de l' Univ. Lyon,* **1,** 18 (1906).

[18] Cumming and Gilchrist, *Trans. Faraday Soc., 9,* 174 (1913).

[19] Lewis and Sargent, THIS JOURNAL, 31,363 (1909).

[20] Lewis, Brighton and Sebastian, *ibid.,* 39, 2253 (1917).

to the liquid junction and to salt effects, the electrode potentials canceling. Second, the diffusion potentials were as great as or greater than those ever encountered in ordinary practice unless more concentrated solutions of a strong acid be used. Third, when the bridge solution was *3.5 N* potassium chloride the junctions were exactly of the type usually encountered in PH measurements. Finally, in some of the measurements, the technique used required that the whole system should be closed; this precluded the use of a hydrogen electrode. On the other hand, the cells had the definite disadvantage that the calomel electrode in acid solution is appreciably affected by oxidation.[21] No very great importance is therefore attached to the absolute values of the e. m. f. measured, owing to uncertainty in the electrodes. On the other hand, the relative values obtained are believed to be reliable on the following grounds. During the period of preliminary measurements, March to July 1928, numerous electrodes were prepared and any two electrodes, which should be identical, never differed by more than 0.4 mv. and only rarely by more than 0.2 mv. None of the measurements made during this early period are reported here as it is uncertain to what extent lack of reproducibility may have been due merely to unskilled technique. All the measurements reported were made between September, 1928 and February, 1929 inclusive. The same calomel–potassium chloride half element was used in all the measurements; three calomel–hydrochloric acid half elements were used; all four half elements were prepared on August 28, 1928. The three calomel–hydrochloric acid elements were compared with one another at intervals; they were also compared with a fourth similar half element prepared on November 10, 1928. The greatest difference ever observed between any two of the three half elements used was 0.20 mv., whereas the greatest difference ever found between one of these and the fourth one was **0.33** mv. We shall see that these fluctuations due to the electrodes are of the same order of magnitude as those in the measured e. m. f.'s of the cells with junctions of a reproducible type; it has therefore seemed most reasonable to apply no correction for the differences between the three calomel–hydrochloric acid electrodes used. That the hydrochloric acid electrodes did not change appreciably relatively to the potassium chloride electrode during the five months in which the measurements were made is shown by the reproducibility of the e. m. f. measured at different times with the same type of junction. The author considers that the measurements justify belief in a reproducibility of about 0.2 mv. when the junction is made in a suitable way.

The half element vessels used were a slight modification of that designed by Lewis, Brighton and Sebastian.[20] As may be seen from Fig. 1, the significant addition is the stopcock, A, which can be connected to a

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

reservoir so that liquid may be sucked up the side-tube B. The extra stopcock in the circuit between E and B has been dispensed with. At C there is a junction by means of a piece of rubber tubing; this makes it possible to clean the side-tube and stopcock A without disturbing the electrode. D is merely a trap for air bubbles and is probably unnecessary

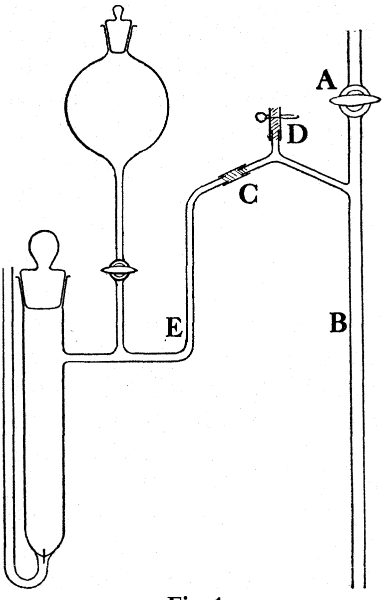

Fig. 1.

All measurements were made with the electrode vessels in a water thermostat at 18°, in which the temperature fluctuations were not more than 0.01°. The liquid–liquid junctions were either in this same water thermostat or in an air thermostat at 18 ± 0.3°, according to the type of junction. Furthermore, the temperature of the whole room was automatically regulated so that the air around the thermostats was generally very near 18° and never deviated by more than 1°.

The measurements were made with a potentiometer constructed by Wolff and a mirror galvanometer made by Siemens and Halske. A Weston normal cell was used as standard. The thermostat and all the electrical apparatus were virtually in an earthed "cage." The electrical equipment could easily measure to an accuracy of 0.01 mv., but in general readings were made correct to 0.1 mv. or 0.05 mv. only.

The cells measured contained in general two liquid–liquid junctions, one between potassium chloride solutions of concentrations 0.1 N and c, the other between potassium chloride of concentration c and 0.1 N hydrochloric acid. According to theory the potential difference across the former should be independent of the method of forming the junction and easily reproducible. This was to some extent confirmed by measuring the symmetrical cells

$$Hg \mid HgCl \mid 0.1\,N\,KCl \mid c\,KCl \mid 0.1\,N\,KCl \mid HgCl \mid Hg$$

The junctions were made by simply dipping the side tubes of the two electrode vessels into a U-tube containing potassium chloride at concentration c. Generally a small e. m. f. less than 0.2 mv. was observed and this was found to be independent of the concentration c of the bridge potassium chloride and unaffected by stirring with an accuracy of 0.01 mv. On the strength of this no special pains were taken in making the junction between the two potassium chloride solutions, as the reproducibility of the e. m. f. is determined by the nature of the other junction.

"Continuous **Mixture** Junction."—This junction, unlike the "constrained diffusion" and "free diffusion" junctions, is theoretically unstable and will be disturbed by diffusion. The instability can be minimized by making the mixture layer long. since the time required for diffusion to annihilate deviations from the steady state conditions is proportional to the square of the distance through which these deviations are initially present. Bjerrum[16] in 1911 stated that the time required was proportional to the first power of this distance, but he now[22] agrees that this was an error. As already emphasized, the "continuous mixture" junction cannot be made merely by stirring, as this procedure may do no more than replace one junction by two of equally indefinite type. The method adopted is shown diagrammatically in Fig. 2. B is the side-tube of the electrode vessel; from C to D is a rubber connection. Initially the cocks A and E are open and the system is filled with 0.1 N hydrochloric acid from F to *G*, the quantity of solution in the beaker H being only a few cc. The mechanical stirrer I is started. Into the beaker H is slowly poured about 10 cc. of a mixture of say 95% 0.1 *N* hydrochloric acid and 5% of c potassium chloride containing one drop of methyl orange solution. Then successive 10-cc. portions are added of mixtures 0.1 N hydrochloric acid and c potassium chloride, the proportion of the latter increasing steadily until eventually pure c potassium chloride was being added. By the time the beaker was full the concentration of hydrochloric acid in it was quite negligible compared with that of the potassium chloride. The diameter of Tube K was so chosen that when the beaker was full liquid had been sucked nearly up to L. This could be seen clearly owing to the drop of indicator added. In the case of the more concentrated potassium chloride solutions there was no difficulty whatever in preparing a mixture layer in this way, but with 0.1 N potassium chloride there was a tendency for the liquid added to the beaker to stream up into the tube B, if the temperatures of the solutions used were a fraction of a degree above 18°. The 0.1 N potassium chloride solution when not in use was, therefore, kept in the air thermostat. The mixture layer having been prepared in this way, the procedure taking rather less than ten minutes, the stirrer was stopped, the stopcocks A and E were closed, rubber tubing disconnected at C and the electrode vessel placed in the water thermostat with the side-tube B dipping into a U-tube containing a potassium chloride solution of concentration c, into the other end of which dipped the calomel–potassium chloride electrode vessel. The U-tube was also in the water thermostat so that all parts of the circuit, where there were concentration gradients, as well as both electrodes, were in the water thermostat. The e. m. f. of the cell was then observed at intervals extending over several hours. In Table I are given the results of four typical sets of measurements; the first three were made with three different calomel–hydrochloric acid electrodes, while the fourth was made on a different day with the same electrode as the first. The times are measured from the returning of the electrode vessel to the water thermostat after the preparation of the mixture layer.

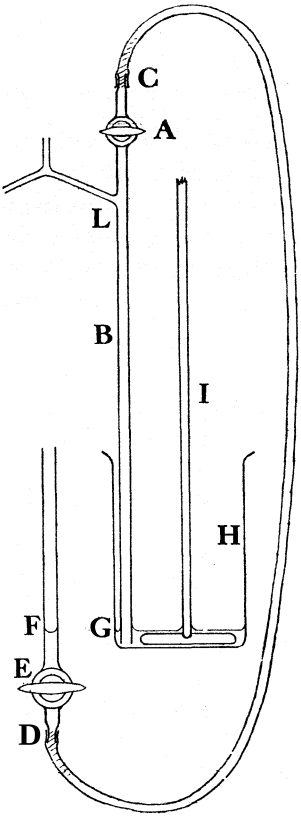

Fig. 2.

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[22] Private communication.

TABLE I

"CONTINUOUS MIXTURE" JUNCTION. BRIDGE SOLUTION 1 N POTASSIUM CHLORIDE

Electrode 1		Electrode 2		Electrode 3		Electrode 1	
Time, min.	E. m. f., mv.	Time, min.	E. m. f., mv.	Time, min.	E. m. f., mv.	Time, min.	E. m. f., mv.
0	7.9	0	7.7	0	7.7	0	7.7
13	8.25	14	8 3	24	8.2	10	8.0
27	8.4	38	8.5	50	8.35	21	8.1
51	8.45	64	8.55	96	8.45	35	8.2
77	8.5	110	8.65			59	8.25
123	8.6						
311	8.75	298	9.2	284	8.6		

For each concentration of the bridge solution at least nine such sets of measurements were made, generally three sets with each of the three electrodes. It was found that the e. m. f. rose generally about a half millivolt in the first ten minutes, but after that only about a quarter millivolt in the next two hours. If we neglect the readings in the first ten minutes and give equal weight to all readings in the next two or three hours, the

TABLE II

EXPERIMENTAL OBSERVATIONS

Concn. of bridge KCl	Mean E. m. f., mv.	R. M. S. dev. in mv.	No. of measurements	Date
	A. "Continuous Mixture Layer"			
0.1	27.4	0.11	39	......
0.2	20.9	.16	31	......
0.5	13.05	.24	33	......
1.0	8.3	.09	20	Early Sept., 1928
1.0	8.3	.11	12	Late Oct., 1928
1.0	8.3	.24	33	Jan., 1929"
1.75	4.9	.14	32	......
2.5	3.1	.19	35	......
3.5	1.55	.11	34	......
	B. "Free Diffusion Junction"			
0.1	27.0	0.24	23	Nov., 1928
0.2	19.95	.11	22	Nov., 1928
0.5	12.55	.18	23	Nov., 1928
1.0	8.9	.17	30	Oct., 1928
1.0	8.4	.18	26	Dec., 1928
1.0	8.4	.28	15	Feb., 1929
1.75	5.15	.14	26	Nov., 1928
2.5	3.4	.21[b]	31	Dec., 1928
3.5	1.1	.15	17	Nov., 1928

[a] The measurements given in detail in Table I are taken from this set; from the value of the R. M. S. deviation it can be seen that the set chosen for illustration is one of the least favorable as regards reproducibility.

[b] One reading after the lapse of ten minutes has been neglected in a case where obviously the steady state was far from reached. Its inclusion would increase the R. M. S. deviation to 0.24 mv.

results given in Table IIA are obtained. The first column gives the concentration of the bridge potassium chloride solution, the second the mean value of the measured e. m. f. in millivolts, the third the root mean square deviation of the individual readings from the mean and the fourth the number of readings made after the first ten minutes. From the dates given in the last column it is clear that there has been no serious change in the electrodes over the whole period during which these measurements were made. These results show that the junction prepared in this way is reproducible with a probable error of less than 0.2 mv. It is noteworthy that the order of magnitude of this uncertainty is independent of the absolute value of the total measured e. m. f.

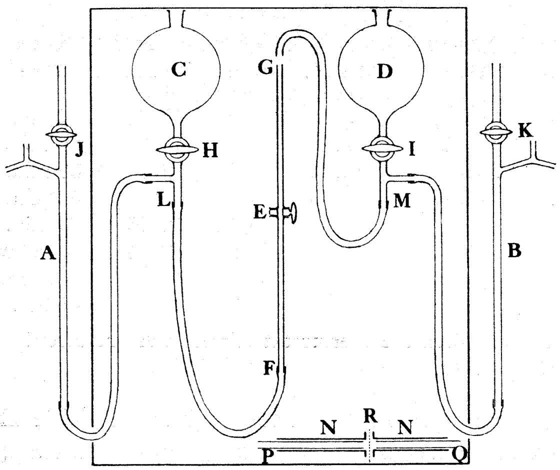

Fig. 3.

"Free Diffusion Junction."—The method of preparing a junction of this type is very simple and is shown diagrammatically in Fig. 3. A and B are, respectively, the side tubes of the calomel potassium chloride and calomel hydrochloric acid half element cells. C and D are reservoirs filled, respectively, with potassium chloride of concentration *c* and with 0.1 N hydrochloric acid. The cock E has the same bore (2-mm. diameter) as the tube FG A rectangle surrounds that part of the apparatus which was within the air thermostat, the electrodes being in the water thermostat. Suppose all cocks initially closed; then on opening E and the reservoir cock on the calomel–potassium chloride electrode vessel (see Fig. 1) 0.1 N potassium chloride will flow from J to ***G;*** the cock on the electrode vessel is then closed and the cock H opened; potassium chloride of concentration *c* then flows from H to G, displacing the 0.1 N potassium chloride; we then have a junction between the two potassium chloride solutions at the T-piece just below the cock H. The cock E is closed, after which the tube from E to G is thoroughly rinsed and then filled with 0.1 N hydrochloric acid by means of a capillary pipet. The whole of the apparatus to the right of G being filled with 0.1 *N* hydrochloric acid, the cock I is opened and while solution is trickling out of the rubber tubing at G, this is connected to the upper end of the tube FG. By opening and closing again the cocks J and K, one can make sure that the pressure difference across the cock E is not more than a few mm. of water. After an interval of about twenty minutes for temperature equilibrium to be obtained, the thermostat stirrers are stopped to avoid vibration and the cock E carefully opened. A "free diffusion junction" is thus formed at the upper end of the cock E. The thermostat stirrers were restarted generally after about half an hour, the transition layer by that time being presumably long enough not to be seriously disturbed by slight vibration. It was found that the time taken for the e. m. f. to reach a steady value varied from a few minutes to about three-quarters of an hour; this corresponds to initial accidental deviations from sharpness extending over a length of the order of 0.5 mm. Once the steady value was reached, it did not vary more than a few tenths of *a* millivolt over a period of twenty-four or even forty-eight hours. Examples of four sets of measurements are given in Table III. The times are measured from the opening of the stopcock E. The reproducibility is even better than in the case of the continuous mixture junction and the stability much greater, as it should be according to theory.

TABLE III

"FREE DIFFUSION JUNCTION." BRIDGE SOLUTION $N/2$ POTASSIUM CHLORIDE

Time, min.	E. m. f., mv.	Time	E. m. f., mv.	Time, min.	E. m. f., mv.	Time	E. m. f., mv.
21	12.45	18 min.	12.35	10	12.75	14 min.	12.5
56	12.5	33 min.	12.35	20	12.9	29 min.	12.55
57	[a]	95 min.	12.55	37	12.9	30 min.	[a]
89	12.45	18 hrs.	12.75	39	[a]	53 min.	12.3
108	12.5			62	12.45	73 min.	12.35
				105	12.55	3.5 hrs.	12.7
						4.5 hrs.	12.75
						45 hrs.	12.8

[a] Denotes the time when the thermostat stirrers were restarted. In the second experiment they were never stopped.

A summary of all measurements made is given in Table IIB. For the sake of consistency all readings taken after more than a quarter of an hour are included, though in a few cases the steady state had not been quite reached in this time. The first column gives the concentration c of the bridge potassium chloride, the second the mean of all readings taken after more than a quarter of an hour, the third gives the root mean square deviation of the individual readings from the mean, the fourth the number of individual readings and the last the date when the set of measurements was made. It will be seen that the probable error in the liquid–liquid junction e. m. f. is again no more than 0.2 mv. and its order of magnitude is independent of the absolute value of the whole measured e. m. f. Cells with 1 N potassium chloride as bridge were measured in October, 1928, December, 1928, February, 1929; the last two sets of measurements are in good agreement, but the first gives an e. m. f. 0.5 mv. higher. This discrepancy has not been explained, but it is to be noted that the measurements in October, 1928 were the first of their kind.[23]

[23] There is now reason to suspect a deficiency in the air-thermostat. In later measurements in collaboration with Miss Unmack the erratic fluctuations have been reduced to 0.1 mv. by improving the control of the temperature of the junction.

In Figure 4 the value of the e. m. f. has been plotted against the concentration of the bridge potassium chloride, the latter on a logarithmic scale to reduce the curvature and so facilitate interpolation. The "continuous mixture layer" points fall on a smooth curve; so do the "free diffusion" points, if for 1 N potassium chloride the October, 1928 value be rejected and the two later sets of measurements taken as correct. The maximum difference between the two types of junctions is just under 1 mv. for 0.2 N potassium chloride; for concentrations of potassium chloride above 1 N it is probably less than the experimental uncertainty.

It is worth noticing that in the case of 0.1 N potassium chloride the value for the "free diffusion" junction is less than that for the "continuous mixture" layer by 0.4 mv. as compared with 0.33 mv. computed by Taylor. While we attribute less certainty to our absolute values than to the relative values, it is, however, satisfactory to find how well they too agree with values computed by Taylor, taking account of salt effects by a semi-empirical intrapolation formula. For the case of 0.1 N potassium chloride Taylor computes the values 27.9 mv. for the "continuous mixture" layer and 27.6 mv. for the "free diffusion" junction at 25°. The observed value of Lewis, Brighton and Sebastian,[20] 27.8 mv., lies between these, while that of MacInnes and Yeh,[11] using the flowing junction, 26.8 mv., deviates by a whole millivolt. The corresponding computed values for 18° are 27.2 mv. (C. M.) and 26.9 mv. (F. D.) in excellent agreement with our observed values 27.4 mv. (C. M.) and 27.0 mv. (P. D.).[24]

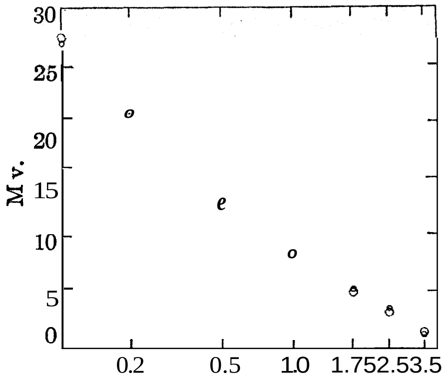

Fig. 4.—0, Continuous mixture layer; o, free diffusion.

A few measurements were made on the "free diffusion junction" by a different technique involving the use of agar-agar. Into a U-tube of height **22** cm. and bore **5** mm. in diameter was poured a hot solution of 1 N potassium chloride containing 3% agar-agar until the tube was approximately half full; the solution was left to congeal on cooling. The upper halves of the two limbs of the U-tube were then filled, respectively, with 0.1 N potassium chloride and 0.1 N hydrochloric acid. The two limbs were then connected to the two electrode vessels by rubber tubing filled with the respective solutions. The U-tube was immersed in the water thermostat and measurements were made. Table IV contains all the measurements. It will be seen that within ten minutes the e. m. f. reaches the value 8.9 mv. and then does not increase by more than half a millivolt in a

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[24] This agreement is now believed to be fortuitous. The absolute value of the e. m. f. of this cell will be discussed in a forthcoming publication by Miss Unmack and the present author.

whole week; this type of junction is the most stable used and the reproducibility is also as good as that of any other type. The mean value, 9.1 mv., of the e. m. f. is 0.7 mv. higher than that of the corresponding junction measured by the former method. The difference may well be due to the effect of the agar-agar on the mobility of the ions, in particular the hydrogen ion.

TABLE IV

"FREE DIFFUSION JUNCTION" WITH AGAR-AGAR

Bridge solution 1 *N* KCl + 3% agar-agar

Time	E. m. f., mv.	Time, min.	E. m. f., mv.	Time	E. m. f., mv.	Time	E. m. f., mv.
0 min.	8.45	2	8 25	2 min.	8.0	2 min.	8.3
2 min.	8.65	9	8.7	34 min.	8.9	20 min.	8.9
11 min.	8 9	29	8.95	52 min.	8 95	100 min.	9.05
41 min.	9.1	35	9 1	75 min.	9.0	7 hrs.	9.1
81 min.	9.15	129	9 1	103 min.	9.05	24 hrs.	9.2
106 min.	9.2			126 min.	9.05	2 days	9.2
20 hrs.	9.35			215 min.	9.1	3 days	9.25
				285 min.	9.1	4 days	9.3
				2 days	9.2	5 days	9.35
						7 days	9.4

Mean 9.1. "R. M. S." deviation, 0.14.

"Constrained Diffusion Junction."—It was suggested by Bjerrum (in 1911)[16] that this type of junction might be realized if the transition layer were within a membrane kept washed on the two sides by the two extreme solutions. The apparatus used is similar to that used for the "free diffusion junction" except for the middle portion between G and F and is shown in Fig. **3**. R is a collodion membrane, on each side of which is a rubber washer; the two outer tubes N are held together by rubber bands round small hooks; the inner horizontal tubes P, Q are, respectively, connected by rubber tubing to the T pieces I, and M and take the place of the vertical tube FG. The cocks H, I are open and by means of screw clamps the rate of flow of the solutions from C, D into the two surfaces of the membrane is regulated.

It was found that the e. m. f. measured with this apparatus was rather sensitive to changes in the rate of flow, but much more to appreciable differences in the rates on the two sides than to the absolute rates. By using as membrane one obtained from Gottingen (denoted as "Membranfilter Fein") and making the rates as nearly as possible equal on the two sides and from about one drop per second to one drop per ten seconds, values were obtained for the e. m. f. fluctuating over a range of about 1 mv. A rough computation by means of Helmholtz' formula as corrected by Perrin,[25] shows that the effect of a possible electrokinetic potential must be quite negligible. The fluctuations observed were presumably due to the transition layer's sometimes being in motion, so that the boundary conditions corresponding to Planck's formula were not accurately fulfilled. All these measurements are summarized in Table V. The first entry gives the number of times the rates of flow were adjusted, the second the total number of readings made, the third the mean e. m. f. and the

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[25] Perrin, *J. chim. phys.*, 2,611 (1904).

fourth the root mean square deviation of the individual readings from the mean. It will be seen that this method is two to three times less accurate than the two types of junctions previously described. The mean value obtained for the e. m. f. is only 0.2 mv. higher than that given by either of the other two types of junction. The value calculated by Planck's formula, neglecting salt effects, was 0.8 mv. higher than the value for the "continuous mixture" junction; the remaining *0.6* mv. discrepancy may be partly due to salt effects and partly experimental error.

TABLE V

"CONSTRAINED DIFFUSION JUNCTION" BY MEANS OF MEMBRANE

Bridge solution 1 *N* KCl

Number of cells...............	18	Mean e. m. f. in mv..........	8.5
Number of readings............	45	"R. M. S." deviation........	0.42

"Sharp" Junctions of Indefinite Type.—Apart from the experimental realization of junctions of the "continuous mixture," "free diffusion" and "constrained diffusion" types, a few measurements were made on "sharp" junctions of the indefinite type in general use. The instability and irreproducibility reported by other investigators were completely confirmed in the case of a junction between two different electrolytes at different concentrations. In Table VIA are given some typical measurements of the cell

$$Hg \mid HgCl \mid 0.1\ N\ HCl \mid 1\ N\ KCl \mid 0.1\ N\ KCl \mid HgCl \mid Hg$$

in which the junctions were made simply by dipping the side tubes of the electrode vessels into a U-tube containing the bridge solution. Table VIB gives some similar examples in which the side-tubes were plugged

TABLE VI

JUNCTIONS OF INDEFINITE TYPE

Bridge solution 1 *N* KCl

Time	E. m. f., mv.	Time	E. m. f., mv.	Time	E. m. f., mv.	Time	E. m. f., mv.	Time	E. m. f., mv.
				A. Side-tubes dipped into bridge solution					
8 min.	10.3	8 min.	6.4	8 min.	9.2	0 min.	8.4	0 min.	8.95
35 min.	11.4	35 min.	7.3	35 min.	11 35	? min.	9 2	? min.	9.9
76 min.	11.8	76 min.	8.1	76 min.	12.4	28 min.	10.4	28 min.	12.2
128 min.	11.9	128 min.	8.5	128 min.	12.95	73 min.	11 0	73 min.	13.1
5 hrs.	11.95	5 hrs.	9.2	5 hrs.	13.0				
21 hrs.	11.65	21 hrs.	10.2	21 hrs.	11.3				
				B. Junction with cotton plugs					
0 min.	10.2	0 min.	11.8	0 min.	12 2	0 min.	11.3	0 min.	10.8
5 min.	11.95	5 min.	13.4	5 min.	12 65	17 min.	12.7	17 min.	12.9
36 min.	12.8	36 min.	13.35	36 min.	14 0	51 min.	12.75	51 min.	12.55
61 min.	12.85	61 min.	13.2	61 min.	14 1	75 min.	12.7	75 min.	12.35
123 min.	12.8	123 min.	12.85	123 min.	14.15	115 min.	12.65	115 min.	11.6
				C. Junction drawn up into side-tube					
0 min.	9.0	0 min.	8.5	8 min.	8.5	3 min.	8 65	0 min.	8.85
3 min.	8.8	7 min.	8.6	41 min.	8.55	36 min.	8.65	6 min.	9.2
21 min.	8.8	32 min.	8.85	130 min.	8.6	125 min.	8.7	24 min.	9.45
83 min.	8.8	60 min.	8.9	20 hrs.	8.85	20 hrs.	9.9	86 min.	9.7
139 min.	8.85							142 min.	9.8

with cotton wool before immersion in the U-tube. The times are measured from the moment of immersion of the side-tubes into the U-tube containing the 1 N potassium chloride. A glance at these tables is sufficient to show that there are irregular fluctuations of the order of several millivolts. The "sharp" junctions made in this way do not correspond to any definite conditions for a steady state and so would not be expected to give good reproducibility. It is nevertheless striking that the fluctuations in the "sharp" junction are so much greater than the greatest differences between the three reproducible types of junction studied. In fact the values obtained for the e. m. f. with the "continuous mixture" and "free diffusion" junctions rarely differed by more than 0.5 mv. and in the particular case of 1 N potassium chloride as bridge they were practically identical. This seems to show that for this particular junction the difference between "free diffusion" layer and the "continuous mixture layer" is insignificant. If the only cause of indefiniteness in the "sharp" junction was the variability in the relative importance of the parts played by diffusion and by mixture in the formation of the transition layer, it would be difficult to explain why the fluctuations with the "sharp" junction should be more than a tenth of what they actually are. There is, however, a characteristic difference between, on the one hand, the three reproducible types of junction discussed from a theoretical point of view and on the other the ordinary "sharp" junction; in the former it is assumed that there is cylindrical symmetry, that is to say, that all concentration gradients are along one and the same direction, while this is far from the case in the latter, where the junction is at the tip of the side-tube of the electrode vessel. The equipotential surfaces in the latter will be highly curved and will depend not only on the exact size and shape of the tip of the side-tube, but also on its position relative to the walls of the U-tube into which it dips; the conditions are altogether too complex for theoretical discussion. It would thus appear that cylindrical symmetry is the most important requisite for reproducibility. To test this suggestion some measurements were made in which the junction was drawn up into the side-tube of the electrode vessel. The transition layer would thus be indefinite as regards the relative parts played by mixture and diffusion, but would approach cylindrical symmetry, though the symmetry might not be complete because the solution when being drawn up the side-tube would probably stream faster in the center than along the walls of the tube. A large number of measurements were made with the junction made in this way and it was found that in most cases a reproducibility of a few tenths of a millivolt was obtained, but once in a while much larger deviations of over a millivolt might occur. Table VIC illustrates one set of nine experiments; the four not recorded were quite similar to the first three in the table; the fourth in the table is also in good agreement for a few hours, but by the next day it has lost its stability; the fifth is typical of the occasional exception. This method of making a junction has been previously used in this Laboratory by Bjerrum and Unmack[26] with very similar results. It is no doubt a great improvement on the usual method and the reproducibility is quite good, if sufficient measurements are made to make the "exceptions" insignificant. The cause of the occasional exception is presumably in the setting up of streams or vortices when the solution is being drawn up into the side tube; these might completely destroy the cylindrical symmetry of the transition layer.

Since the completion of the rest of the present research, the author has been making measurements with hydrogen electrodes in collaboration with Miss Unmack. We made a few experiments in which cylindrical symmetry was deliberately avoided, as, for example, by making the two solutions meet at the junction of two tubes of different bore. The resulting e. m. f.'s were erratic to the extent of several millivolts, even though one of the solutions was **3.5** *N* potassium chloride.

Conclusion

Owing to considerations of salt effects discussed elsewhere[27] the absolute values of the e. m. f. measured are of little interest as they give no simple information of thermodynamic interest. It was partly for this reason that no great pains were taken over the preparation of the electrodes beyond having three calomel–hydrochloric acid electrodes that agreed amongst themselves. It has been shown that cells with liquid junction give reproducibility comparable with that of cells without liquid junction, but only when the transition layer is of such a type that reproducibility can be expected from theoretical considerations. Perhaps the most interesting quantitative result of the measurements is that as long as there was cylindrical symmetry the free diffusion junction gave values for the e. m. f. differing generally by only a few tenths of a millivolt from that given by the continuous mixture layer. This would probably no longer be the case for a junction between concentrated hydrochloric acid and dilute potassium chloride, but for the commonest type of junction, *3.5* N potassium chloride against a much more dilute solution, it seems not unlikely that the difference will be small. Hence in computations of the liquid junction potential, salt effects being neglected, it may be allowable to use the formula corresponding to a "continuous mixture layer" even if the actual junction is of the "free diffusion" type.

In a recent paper of great interest MacLogan[28] gives the results of a purely experimental study of the cell.

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[26] Bjerrum and Unmack, *Kgl. Danske Videnskab. Selskab Math.-fys.* **Medd.** [1] 9, (1929).

[27] Guggenheim, J. *Phys. Chem.*, **36,** in press.

[28] MacLogan, *Biochem. J.*, 23,309 (1929).

Hg | HgCl | 0.1 N HCl | sat. KCl | 0.1 N KCl | HgCl | Hg

He finds in complete agreement with our own results that the important condition for both reproducibility and stability is that the junction should be within a tube and not at its tip.

The author would like to express here his gratitude to Professor Bjerrum for his invaluable advice and encouragement, as well as his friendly criticism; he is also indebted to the Rask-Ørsted Foundation for the award of a grant.

Summary

1. The diffusion potential between two ideal dilute solutions of different electrolytes or mixtures of electrolytes depends on the nature of the transition layer between the two end solutions.

2. The "continuous mixture" layer should give a reproducible potential difference, corresponding to Henderson's formula, but it is theoretically unstable. The instability can be minimized by making the transition layer sufficiently long. This has been realized experimentally and an e. m. f. obtained reproducible and constant to within 0.2 mv. over several hours.

3. The "constrained diffusion" junction with cylindrical symmetry represents a steady state with a transition layer of unchanging length. The potential difference is given by Planck's formula and is independent of this length. It is difficult to realize experimentally, a reproducibility of only 0.4 mv. having been obtained.

4. In the "free diffusion" junction with cylindrical symmmetry the transition layer increases in length proportionally to the square root of the time, but the potential difference should not change. It is easy to realize experimentally and an e. m. f. has been obtained reproducible and constant to within 0.2 mv. over at least twenty-four hours. Unfortunately there is no formula giving the potential difference explicitly, the general validity of Taylor's approximate treatment being questionable.

5. The "sharp" junction is theoretically indefinite. Experiment confirms this by giving e. m. f. values fluctuating over several millivolts when there is not cylindrical symmetry.

6. The "flowing junction" is either a special case of the "continuous mixture layer" or else represents *a* steady state determined by the shape of the apparatus used and so too complicated for theoretical discussion. It is generally assumed to be the former.

7. In the cell

Hg | HgCl | 0.1 N HCl | *c* KCl | 0.1 N KCl | HgCl | Hg

where *c* varies from **0.1** to 3.5, as long as the transition layer has cylindrical symmetry, the e. m. f. obtained never differs by more than a few tenths of a millivolt from that given by the "continuous mixture" junction.

On the other hand, irregular fluctuations of several millivolts are obtained when the junction is at the end of a thin tube dipping into a wider one.

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COPENHAGEN

[CONTRIBUTION PROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

PREPARATION OF NEGATIVE COLLOIDAL FERRIC OXIDE BY HYDROLYSIS OF PRUSSIAN BLUE

BY FRED HAZEL AND C. H. SORUM

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Hydrolysis of a solution of ferric chloride yields a positive ferric oxide sol. In order to account for the character of the electrical charge on this sol, Powis[1] offers the following explanation. While both ferric ions and chloride ions are adsorbed by the colloidal particle, the former are preferentially adsorbed, and since they are relatively more positive than the chloride ions are negative, the micelle acquires a positive charge. The same author points out the fact that, in general, colloidal suspensions of the hydroxides of multivalent metals are positive. This is because they are prepared by dialysis or hydrolysis of one of their salts having a univalent anion.

Frequent mention is made in the literature of negative colloidal ferric oxide.[2] The general methods of preparation have consisted, in the main, of operations in one or in two steps. In the latter case a positive sol is prepared and then recharged by allowing it to come into contact with a solution containing some negative ion which is sufficiently adsorbed to give to the micelle a negative charge. The other mode of operation, while essentially the same, is different in that the positive form is not isolated but is recharged in the same system in which hydrolysis is performed. Thus Powis[1] prepared negative ferric oxide by allowing a dilute solution of ferric chloride to flow into an excess of sodium hydroxide solution.

Von Kohei Hakozaki[2] has shown that positive colloidal iron oxide can be recharged negatively by the addition of potassium ferrocyanide. The tetravalent ferrocyanide ions are not only highly negative but they also have a large volume and are probably only slightly hydrated. The last two factors enable these ions to be strongly adsorbed and the first likewise contributes to make them very effective in reversing the charge on a positive iron oxide sol. From these facts it was suggested to us that if hy-

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[1] Powis, **J.** *Chem. Soc.*, *107*, 818 (1915).

[2] **Fischer,** *Biochem. Z.*, **27,** 223 (1910); **Dhar and Sen, J.** *Phys. Chem.*, 27, 376 (1923); **Dhar, Sen and Gosh,** *ibid.*, 28,457 (1924); **Kruyt and van der Spek,** *Kolloid-Z.*, **22,** 81 (1918); 25, **17** (1919); **von Kohei Hakozaki,** *ibid.*, 39,319 (1926).

drolysis of a ferric salt in the presence of this easily adsorbable highly negative ion could be achieved, a negative iron oxide sol might result.

Ferric ferrocyanide was selected as the salt to be hydrolyzed on the strength of the following observations. When a dilute solution of ferric chloride is dropped into a boiling solution of potassium ferrocyanide, a deep blue negative sol of Prussian blue results. Similarly, a negative sol of Prussian blue is obtained when small crystals of the salt are shaken with cold water. Apparently Prussian blue is soluble enough to give Fe^{+++} ions and $Fe(CN)_6^{----}$ ions, which, on being adsorbed by the molecules of $Fe_4[Fe(CN)_6]_3$, yield a negative colloid. In verification of this assumption it was found that by making a fresh dilute suspension of Prussian blue in water and dropping this suspension slowly into five liters of vigorously boiling distilled water the resulting product first became bluish, then faded to colorless or pale yellow. The fading indicated the start of hydrolysis of Prussian blue. Further addition of the salt gave a product that changed in color from yellow to orange and finally to a dull red. Tests applied to this red solution proved it to be a negative colloid.

The best results have been obtained by preparation according to the following method. A fresh suspension of *2* g. of Prussian blue is made in one liter of distilled water and allowed to drop slowly into five liters of boiling distilled water. After the addition of the first ten drops the operation is stopped until hydrolysis commences. This action becomes apparent as the color changes from blue to a faint yellow. The initial change from blue to yellow normally requires thirty or forty minutes. However, if a small amount *(5* cc.) of positive or negative colloidal ferric oxide is added to the receiving flask containing the boiling water, the change takes place in less than five minutes. Dropping is resumed after the start of hydrolysis and is continued until the liter of suspension has been added, the complete operation requiring five hours. Boiling distilled water is added at intervals to offset the loss of water resulting from the prolonged boiling. After all of the Prussian blue is added, the sol has become chocolate colored. If it is now allowed to stand for fourteen hours, a slight settling is noted in the bottom of the flask and the sol has changed to a greenish color. Boiling at this point entirely destroys the green color and turns the sol permanently red. The green coloration may be avoided by boiling for thirty or forty minutes after the addition of the last drop of Prussian blue, but there is always a slight settling of a brownish-black residue after the sol has stood for fourteen hours or longer.

The sol prepared in the above manner was dialyzed at a temperature of 80–90° for twenty-four hours. It showed no signs of settling at the end of this period and only a slight trace of settling was shown after the dialyzed sol had stood for three weeks. However, excessive dialysis produced instability. Thus, after five or six days of cold dialysis or three days of hot dialysis, the sol flocculated.

In appearance the stable sol is somewhat cloudy in reflected light but is red and perfectly clear in transmitted light providing the Prussian blue has been added at a slow rate. If addition of the salt has been too rapid, *i. e.,* less than five hours has been required for the complete operation, the sol is turbid in transmitted light. Qualitative analysis of the coagulum from the turbid sol for nitrogen by the sodium fusion test shows the element to be present. However, analysis of the clear sol gives no evidence of nitrogen. In the latter case it may be assumed that hydrolysis is complete, the final product being, most likely, hydrated ferric oxide. Similarly in the case of the turbid sol it may be assumed that hydrolysis is incomplete, there being present in the final product both ferric oxide and complex iron cyanide compounds.

The particles of the clear sol are plainly visible in the ultramicroscope. Using this instrument their mean diameter was found to be $89\mu\mu$ when measured according to the technique developed by Ayres in this Laboratory and to be presented by him in a later communication. Migration toward the anode during cataphoresis indicates that the particles carry a negative charge. The value of the zeta potential was found to be 29.5 millivolts when measured under a potential gradient of 5.11 volts per cm. The method employed in the cataphoretic experiments was a modification of that used by Burton.[3] It was found that by replacing the distilled water in the U-tube above the sol with the ultrafiltrate from the sol better results were obtained.

The following flocculation values were obtained on a sol which contained 0.1 g. of iron per liter and which had been dialyzed at a temperature of from 80 to 88° for twenty-four hours. Since the sol particles are negatively charged, the cation is the effective agent in producing flocculation. ("Flocculation value" as here used denotes the number of millimoles of electrolyte per liter which produced complete flocculation in four hours, the reaction taking place in a volume occupying 4 cc.)

TABLE I

FLOCCULATION VALUES

Electrolyte	$NaCl$	$BaCl_2$	$AlCl_3$
Flocculation value	40.0	0.9	0.045

In Table II an irregular series is shown with thallic chloride, since this salt in its higher concentrations gives a non-flocculating zone where the charge on the sol is positive.

TABLE II

DATA WITH THALLIC CHLORIDE

$ThCl_4$ per liter, mml.	Flocculation	Dir. of migr. in cataphoresis	$ThCl_4$ per liter, mml.	Flocculation	Dir. of migr. in cataphoresis
50	Complete		0.1	Complete	
10	Partial		0.08335	Complete	
5	None	Toward cathode	.0625	Complete	
2.5	None	Toward cathode	.05	Partial	
1.0	None	Toward cathode	.025	Partial	
0.5	None	Toward cathode	.0125	None	Toward anode
0.25	None	Toward cathode	.01	None	Toward anode
0,1667	Complete		.005	None	Toward anode
0.125	Complete				

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[3] Burton, *Phil. Mag.*, [6] **11**, 434 (1906).

The upper flocculation zone corresponds to the flocculation of a positive sol, the lower to that of a negative sol. All those cases in which complete flocculation occurred when 2 cc. of electrolyte was added to 2 cc. of sol and allowed to stand for four hours are listed as the "Complete" flocculation zone under the column headed "Flocculation." All other cases in which complete flocculation occurred or which showed turbidity at the end of seventy-two hours are placed in the "Partial" flocculation zone. "No flocculation" corresponds to the samples in which no turbidity was manifest at the end of seventy-two hours.

A comparison of the properties of this sol is being made with the properties of a sol that has been recharged with potassium ferrocyanide. The effect of H^+ ion concentration on an irregular series for colloidal ferric oxide is being studied using potassium ferrocyanide as the recharging agent.

Summary

1. Negative colloidal hydrous ferric oxide has been prepared by hydrolysis of a suspension of Prussian blue.
2. Some of the properties of the sol have been studied.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

TEMPERATURE–CONDUCTANCE CURVES OF SOLID SALTS. III. HALIDES OF LITHIUM

BY D. C. GINNINGS[1] WITH T. E. PHIPPS

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The temperature–conductance curves of the solid halides of sodium and potassium have been investigated[2,3] and found in most cases to exhibit two distinct slopes when ploited to the axes log k (logarithm of the specific conductance) against $1/T$ (reciprocal of the absolute temperature). It was suggested by one of the writers[2] that the change of slope is probably significant of a change in the mechanism of conduction. Pursuant of this suggestion, transference experiments were performed upon sodium chloride[4] which indicated that only the sodium ion takes part in the conduction process over the temperature range of the lower slope, while in the higher temperature range both ions contribute to the conduction.

With the assumption that the conductance of a solid is proportional to the number of ions in its lattice which have an energy greater than a

[1] This paper is an abstract of a thesis submitted by D. C. Ginnings 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] Phipps and Partridge, *ibid.*, 51, 1331 (1929).

[4] Phipps and Leslie, *ibid.*, SO, 2412 (1928).

certain threshold value, it was shown[2] that the slope of the log $k-1/T$ curve may be interpreted as measuring the "heat of liberation" which the conducting ion or ions must acquire in order to participate in the conduction process. From this point of view the lower slope (*i. e.*, the slope found in the lower temperature range) for sodium chloride measures the "heat of liberation" of a sodium ion in the sodium chloride lattice and the upper slope is a measure of the combined "heats of liberation" of a sodium and a chloride ion.

It was the purpose of this investigation to determine whether the temperature-conductance data of solid lithium halides can be represented satisfactorily by the log $k-1/T$ relation, to compare the conduction process in the lithium halides with that in the sodium and potassium series, and finally to attempt a correlation of the heats of liberation found in the different series.

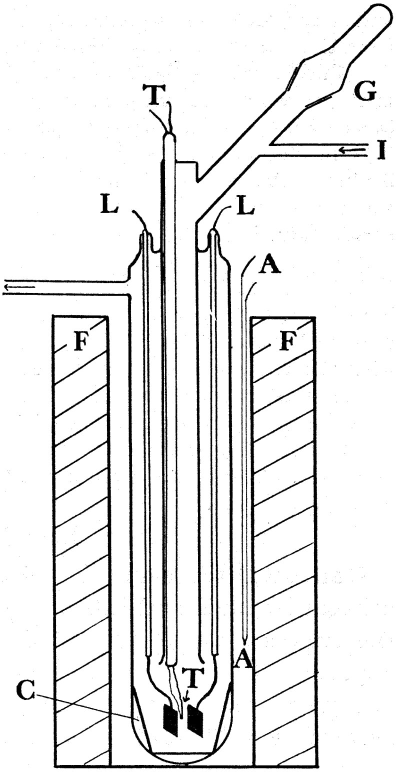

Fig. 1.—Conductivity apparatus.

Experimental

Method and Apparatus.—Because of the extreme hygroscopic character of the chloride, bromide and iodide of lithium, a new method was necessary. In previous work[2,3,4] a crystal or a high-pressure pellet had been clamped between two electrodes, and the conductance had been measured in a furnace open to the air. Two precautions were taken with the lithium halides. First, all water was removed and any lithium hydroxide formed by hydrolysis of the halide at high temperatures was converted back to the halide. This was accomplished by passing dry halogen acid gas over the molten salt for an extended period. Second, no moisture should be allowed to reach the salt. This was accomplished by carrying out all operations in an atmosphere of dry nitrogen.

The apparatus shown in Fig. 1 was constructed of pyrex glass and platinum. The salt was introduced through a ground-glass joint G into the platinum crucible C, which enclosed two platinum electrodes and a platinum–platinum-rhodium thermocouple T. The apparatus was placed in a furnace F, the temperature of which was controlled by a chromel–alumel thermocouple A in conjunction with an automatic temperature regulator made in this Laboratory. The appropriate dry halogen acid gas was passed in at I over the molten salt in the platinum crucible until all moisture had been removed and all hydroxide converted to the halide. The halogen acid gas was then swept out with dry nitrogen and the salt was allowed to cool and form a crystal or conglomerate of crystals around the electrodes and thermocouple.

The electrical conductivity of the salt was measured in much the same manner as in previous investigations.[2,3] An alternating current Wheatstone bridge was used at the higher temperatures for resistances up to one megohm. An alternating current of about 1200 cycles was supplied by a vacuum tube oscillator, and the bridge was designed to conform with suggestions of Jones and Josephs.[5] At lower temperatures, where resistances were greater than one megohm, a direct current deflection method was used. The source of e. m. f. for medium resistances was a potentiometer, and for high resistances, a high voltage "B" battery. The current was measured by a galvanometer having a sensitivity of about 5×10^{-11} amperes per mm. at a scale distance of three meters. To reduce polarization of the crystal the current was passed for only a few seconds at a time and was never allowed to exceed about 10^{-8} amperes.

A platinum–platinum-rhodium thermocouple was used with a Weston Universal potentiometer for measuring the temperature. The thermocouple was calibrated twice during the investigation against the boiling points of water, naphthalene, benzophenone and sulfur, and against the melting point of potassium chloride. A maximum deviation from the standard of about two degrees was observed at the highest temperatures.

Purification of Salts.—On account of the importance of purity of salts in conductance work, extreme care was taken in the preparation of the pure lithium halides. Suggestions by Richards and Willard[6] were followed. Mallinckrodt's "C. P." grade of lithium chloride was the basic material used. This was dissolved, treated with solid lithium carbonate and filtered, to remove a large part of the iron impurity. The chloride was converted to the nitrate and recrystallized several times to remove calcium, magnesium and iron. The nitrate was then converted to the carbonate, dissolved with carbon dioxide as the bicarbonate and reprecipitated as the carbonate by heating. This last reprecipitation was repeated to remove the remaining traces of alkali metal impurities. The pure halides were made by adding the appropriate halogen acid to the pure carbonate. The halogen acids were of C. P. grade, and were redistilled in pyrex, with the exception of hydrofluoric acid which was redistilled in platinum. Spectroscopic tests on the purified salts showed a very faint sodium line in contrast with the exceedingly strong line from the original material.

The melting points of the chloride, bromide and iodide were, respectively, 606, 551 and 467°. The values given in the "International Critical Tables" are, respectively, 613, 547 and 446°.

Experimental Results

General Discussion.—The data for one sample each of lithium chloride, lithium bromide and lithium iodide are plotted in Fig. 2. The slopes of the curves for two samples of each salt are averaged in Table I. It is apparent that there is a break in all the curves. Unlike the behavior observed previously for sodium and potassium halides, evidence appears here of two different lower slopes, one the result of a. c. and the other the result of d. c. measurements. In the case of lithium chloride and lithium bromide the d. c. lower slope differs from the a. c. lower slope by an amount considerably greater than can be ascribed to experimental error; in the case of lithium iodide the two lower slopes are the same. In the case of potassium halides, an anomalous behavior of the a. c. points in the region of transition from the upper to the lower slope has already been commented upon.[3] This so-called "a. c. anomaly" was evident in

[5] Jones and Josephs, THIS JOURNAL, 50, 1049 (1928).

[6] Richards and Willard, *ibid.*, **32**, 4 (1910).

TABLE I

HEATS OF LIBERATION

	$E \times 10^{-3}$ cal. per g, mole (upper slope)	$e_1 \times 10^{-3}$ cal. per g. ion (lower slope)	$e_2 \times 10^{-3}$ cal. per g. ion $(E-e_1)$	T_m, melting point, °K.
LiCl	32.6	13.6	19.0	879"
LiBr	28.0	12.8	15.2	824[a]
LiI	21.2	8.4	12.8	740[a]
NaCl	39.8	20.2	19.6	1077
NaBr	38.4	18.4	20.0	1028
NaI	28.3	13.8	14.5	924
KCl	46.6	22.8	23.8	1043"
KBr	45.4	22.4	23.0	1006"
KI	37.2	19.6	17.6	952"

[a] Experimental values determined for the salts used in these investigations.

larger values of conductance by the a. c. than by the **d.** c. method in the transition region. The same general result is observable here in the lithium series, except that the a. c. values do not deviate as markedly from the extrapolated d. c. slope as was the case for the potassium halides. In the potassium series, there was little doubt that the a. c. anomaly arose from an inherent defect of the a. *c.* method in the transition region. Similarly in the lithium series it is probable that the a. c. lower slope is untrustworthy due to the same defect. Accordingly in Table I the a. c. lower slope is disregarded and the calculations of "heats of liberation" (e_1 values) are made from the d. c. lower slopes.

Heats of Liberation.—The applicability to salt conduction of the van't Hoff relation

$$\frac{d \ln k}{dT} = E/RT^2 \qquad (1)$$

has been discussed in a previous paper.[2] In this equation k is the specific conductance in mhos and E is a quantity of heat.

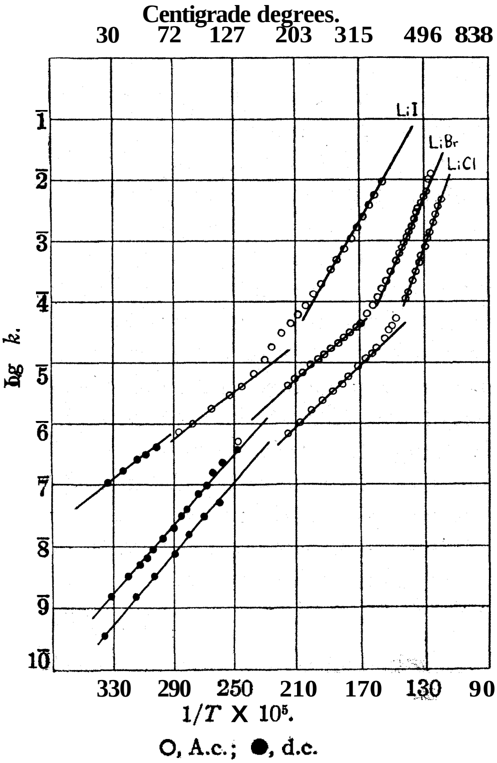

Fig. 2.—Conductance of lithium chloride, lithium bromide and lithium iodide. Only one sample of each is graphed but data on two samples of each salt are averaged in Table I.

This expression may be written

$$E = -R\frac{\mathrm{d}\ln k}{\mathrm{d}(1/T)} \tag{2}$$

E may be interpreted as the "heat of liberation" of a gram-ion of the conducting ion species in a crystal lattice, and d ln $k/\mathrm{d}(1/T)$ is the slope of the conductance curve when plotted to the axes ln k against $1/T$. Equation 2 becomes

$$E = -4.58 \times \frac{\mathrm{d}\log k}{\mathrm{d}(1/T)} \tag{3}$$

where E is given in calories per gram ion.

Table I gives the heats of liberation calculated by Equation 3 from the lower and upper slopes of the three lithium halides. Values from two runs upon each halide were averaged in the table. For purposes of comparison the corresponding values for sodium and potassium halides are presented in the same table. Column 2 gives the values of $E \times 10^{-3}$ in calories per gram mole, as calculated from the upper slopes. Column 3 gives values of $e_1 \times 10^{-3}$ in calories per gram ion (alkali metal ion) as calculated from the d. c. lower slope. Column 4 gives values of $e_2 \times 10^{-3} = (E - e_1) \times 10^{-3}$. The e_2 values are interpreted as "heats of liberation" of the halide ions. Column 5 gives the melting points of the salts used in these investigations.

No data for lithium fluoride are found in this table. Due to its high melting point it was impossible to use the pyrex apparatus utilized for the other halides. Contrary to expectations, it was found to hydrolyze considerably when melted in air and to attack the platinum crucible. When dry hydrogen fluoride gas was passed through the melt the platinum crucible was no longer attacked. However, measurements of the conductance in air were not entirely satisfactory. It soon became apparent that a more refined technique will be necessary. Measurements in the neighborhood of the melting point indicated a very rapid increase in conductance at a temperature above 500°. This behavior is quite similar to that observed with sodium fluoride.[2] Change in crystal form in the neighborhood of the melting point is a possible explanation of this unusual behavior. An independent study of alkali fluorides will probably be undertaken in the future.

Discussion of Results

Table I reveals the following interesting generalizations. I. In a series of alkali halides having a common halogen, the lighter the alkali metal the less is the "heat of liberation" of either the alkali ion or the halide ion in the lattice. This is evident for example in the decreasing values of e_1 and e_2 in the series potassium chloride to lithium chloride.

II. In a series of alkali halides having a common alkali metal, the lighter the halide ion the greater the "heat of liberation" of either the halide ion or the alkali metal ion. This is evident for example in the increasing values of e_1 and e_2 as one goes from lithium iodide to lithium chloride. The exception to this rule in the e_2 value of sodium bromide may possibly be due to experimental error in the sodium series.

III. In the lithium series the relation $E = AT_m + B$ holds quite well. T_m is the melting point in degrees Kelvin and the constants A and B have the values, respectively, 83.6 and -40.8×10^{-3}. In the sodium and potassium series, perhaps due to experimental error in the earlier determinations of E, a linear equation is not adequate.

Summary

The temperature-conductance curves of solid lithium halides have been determined between room temperatures and temperatures near the melting point. Two slopes were found for the lithium halides, a behavior previously observed for the sodium and potassium halide series. This is taken to indicate a similarity in the conduction process in all three series. If this interpretation is correct, the lithium ion alone conducts at lower temperatures and both lithium and halide ions take part in the conduction at higher temperatures.

A comparison of the "heats of liberation" of the conducting ions in the different series, as calculated from the slopes of the conductance curves, has led to three generalizations. In the incomplete lithium series the "heat of liberation" appears to be a linear function of the temperature of the melting point.

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[CONTRIBUTION FROM MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

THE JAMIN EFFECT IN CYLINDRICAL TUBES

BY W. O. SMITH[1] AND MILTON D. CRANE[2]

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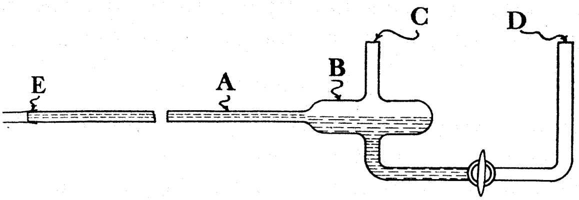
About the middle of the last century Jamin[3] noticed that an ordinary cylindrical capillary tube filled with a chain of alternate air and water bubbles is capable of sustaining a finite pressure. If a series of constrictions is placed in the tube, the pressure sustenance is considerably increased. Each of these two effects, which might be termed the cylindrical and non-cylindrical, respectively, is referred to by Jamin's name. The writers have investigated the former, and conclude from their work that careful cleaning and avoidance of contamination render a cylindrical capillary incapable of sustaining pressure.

[1] Industrial Fellow, Mellon Institute of Industrial Research, Pittsburgh. Pa.

[2] This work was done while the junior author was a senior student in the School of Mines, University of Pittsburgh.

[3] M. J. Jamin, *Compt. rend.*, 50, 172–176,311314,385–389 (1860).

Apparatus.—The device used consisted of a cylindrical capillary about 1 meter long. On one end was fastened a cylindrical glass reservoir 2 cm. in diameter and 10 cm. long. An open water manometer fastened to this reservoir served to measure pressure. A second opening into the reservoir introduced water and fluids. If the reservoir is partly filled and a vacuum is applied to the end of the capillary, a chain can be quickly introduced. The apparatus is shown in Fig. 1.



A, Capillary; C, manometer connection; B, reservoir; D, filling connection; E, ground-glass joint for applying vacuum.

Fig. 1.—Apparatus for producing Jamin chain.

Experimental Procedure.—This apparatus was cleaned with hot chromic acid mixture and was finally washed out by prolonged steaming. Pure water was prepared by distillation from alkaline permanganate solution in a still constructed entirely of hard glass. Its surface tension was found to be 72.2 dynes at 24°. The water was distilled directly into the reservoir described until a quantity sufficient to introduce a chain had been obtained. In general, a chain shorter than the length of the tube was used and placed so as to occupy the portion of the tube adjacent to the reservoir, the remainder of the capillary being open. While the chain was confined within the tube, no pressure could be sustained. However, when a bubble had reached the end of the tube and had formed a meniscus over its plane surface (Fig. 2), small pressures were supported. The pressure p required to overcome this end-resistance is given in order of magnitude by $p = 2\pi r\sigma/\pi r^2 = 2\sigma/r$, where r is the radius of the tube and σ the surface tension of the water. Table I shows the observed and calculated end-pressure for chains of varying lengths. The agreement is well within the limits of error when it is remembered that the end bubble is formed partly exterior to the capillary.

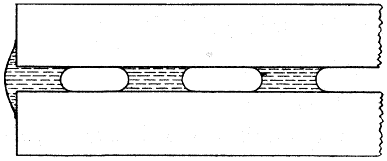


Fig. 2.—Position of bubble at end of capillary.

After drying the inside of the tube by a stream of clean dry air, it was contaminated by being completely filled with a solution of oleic acid in benzene. The filled tube was allowed to stand from thirty minutes to one

TABLE I

END-RESISTANCE FOR UNCONTAMINATED TUBE

Number of bubbles in tube	Length of bubbles Air, mm.	Water, mm.	End-press., cm. of water	Computed end-press., cm. of water	Radius of tube, cm.
118	5–10	2	2.20	2.72	0.054
92	4.5–7	1.5	2.25	2.72	.054
108	4.5–9	1.75	2.22	2.72	.054
120	5–15	1	2.00	2.72	.054
106	4.5–10	1.5	2.20	2.72	.054
110	4.5–10	1	2.05	2.72	.054
117	4.5–10	1	2.05	2.72	.054

hour and was again drained and dried by a stream of clean dry air. The chain of alternate air and water bubbles was then re-introduced, with the result that the column sustained finite pressures ranging from several centimeters to over a meter of water, depending on the concentration of the oleic acid solution used. The data are tabulated in Table II. Relatively small concentrations of oleic acid were found to show a greater sustaining capability than larger ones, but the limits have not been completely investigated. The results reported seem to warrant the conclusion that there is no Jamin effect in cylindrical tubes when perfect wetting liquids are used. However, when there is only partial wetting and hysteretic contact angles are present, there will be a definite effect.

TABLE II

CONTAMINATED TUBE

No. of bubbles in tube	Length of bubble Air, mm.	Water, mm.	Press. obs., cm. of water	Press. per bubble, cm. of water	Radius of tube, mm.	Concn. of contamination soln. (oleic acid in benzene), N
185	2	3	161	0.870	0.54	0.001
149	2–4	1	106	.711	.54	.001
175	2–4	1	48.5	.278	.54	.02
69	1–2	1	12.2	.177	.54	.02

Theory.—Let us consider a single tube containing a chain of alternate air and water bubbles. Let one end be exposed to the atmosphere and the other be acted upon by a pressure P. Then, if n is the number of bubbles, each designated by i, r the radius of the tube, σ the surface tension of the contaminated liquid, Θ_1 and Θ_2 the contact angles on the advancing and receding ends of a bubble, respectively, we have the following equilibrium relation for tubes which are so small that gravity effects are negligible

$$\pi r^2 P - \sum_1^n{}_i\, 2\pi r\, \sigma\,(\cos\Theta_2 - \cos\Theta_1)_i = \pi r^2 A$$

from which

$$P = \frac{2}{r}\sum_1^n{}_i\, \sigma\,(\cos\Theta_2 - \cos\Theta_1)_i + A \qquad (1)$$

where A is atmospheric pressure.

There are several possibilities. It is apparent that, if $\Theta_1 = \Theta_2$, including $\Theta_1 = \Theta_2 = 0$, we have $P = A$, and no finite pressure can be sustained. On the other hand, when $\Theta_1 \neq \Theta_2$, a finite pressure given by Equation 1 can be supported. The greatest pressure P' which can be sustained is given by

$$P' = \frac{2\sigma n}{} (\cos \Theta'_2 - \cos \Theta'_1) + A \qquad (2)$$

where Θ'_2 and Θ'_1 are the extreme values which the contact angles assume. This is obviously produced by increasing the pressure P until all bubbles have suffered their maximum distortion.

Alteration of curvature radii is easily observed, although it cannot be reconciled with the Laplace curvature relation unless hysteresis of contact angles is present. The static problem of capillarity requires the finding of solutions of this equation and adapting them to a given solid boundary for a given angle of contact. If the contact angle is fixed, there is a unique solution, hence a definite curvature.

Discussion.—The results suggest that the hysteresis $(\Theta'_2 - \Theta'_1)$ is determined by the concentration of the contaminating substances present, a slight contamination producing a greater effect than a larger, within a certain range. Another factor, however, is to be considered. One would expect that small concentrations of the contaminating solution contain a sufficient number of molecules to be adsorbed on the glass surface and leave very few to be adsorbed on the water interface after introduction of the chain. Hence, the surface tension of the water is not lowered appreciably. When larger concentrations are used, there is an excess which is adsorbed on the surfaces of the water bubble, lowering its surface tension appreciably. Obviously, from Equation 1, the value of P will be decreased.

In order to verify Equation 2, a detailed study should be made of the manner in which concentration of contaminating solution affects the pressure which can be supported, as well as its relation to contact angles, especially hysteresis. In addition, the variation of σ due to the changed concentrations should be checked.

In conclusion, it must be emphasized that for the case of a non-cylindrical tube, containing a series of constrictions, a definite Jamin action must occur due to the geometrical nature of the boundary, as a simple application of the capillary equation to a completely wetted conical capillary of circular section will demonstrate.

The writers wish to thank Paul D. Foote, Irving Langmuir and W. A. Hamor for advice and suggestions during the progress of this work.

Summary

Two types of Jamin effect are recognized, namely, that occurring in cylindrical tubes, and that in non-cylindrical capillaries. For the cylindri-

cal case, the authors were unable to detect any effect when the tubes were so clean that complete wetting occurred. On contamination of the tubes with solutions of oleic acid in benzene, finite pressures could be supported. Slight contaminations have more effect than larger ones within certain limits. The results suggest that Jamin action arises in cylindrical tubes because of hysteresis of contact angles. The greatest pressure P' which can be sustained is calculated to be

$$P' = \frac{2un}{} (\cos \Theta'_2 - \cos \Theta'_1) + A$$

where Θ'_2 and Θ'_1 are the maximum and minimum values which the contact angles assume, n the number of bubbles in the chain, a the surface tension, r the radius of the tube and A atmospheric pressure.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OF PRINCETON UNIVERSITY]

THE VOLUMETRIC ESTIMATION OF SODIUM

BY EARLE R. CALEY

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The direct gravimetric magnesium uranyl acetate method for sodium, which is satisfactory when only a few sodium determinations are required, does not readily lend itself to making a series of such determinations rapidly. While it is true that colorimetric modifications of this method are capable of fulfilling this requirement, they suffer from the disadvantage of a limited range. The procedure given below is the result of experiments directed toward devising a rapid volumetric method suitable for making a series of sodium determinations.

The principles underlying this volumetric method are simple. The sodium is separated from the other elements in the same manner as described in a previous paper[1] but, instead of drying and weighing the precipitate of sodium magnesium uranyl tri-acetate, the latter is dissolved in water containing 4–5% of acetic acid and the uranium is titrated with a standard solution of sodium phosphate using potassium ferrocyanide as an outside indicator. Under the proper conditions the uranium is quantitatively precipitated as di-uranyl hydrogen phosphate, while the magnesium remains in solution. Since the uranium and sodium contents of this precipitate have been shown to be in fixed, definite ratio when it is formed under the correct conditions, a measure of the sodium present is thus obtained. While the titration of uranium with phosphate solution using an outside indicator is not an especially accurate procedure, the errors involved are greatly divided by reason of the favorable weight ratio (31.07:1) of uranium to sodium in the triple acetate precipitate. The result is that

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[1] Caley and Foulk, THIS JOURNAL, 51, 1664–1674 (1929).

sodium can be quite satisfactorily determined by this volumetric process, as the experimental results show.

Reagents Required

Standard Sodium Chloride Solution.—2.5415 g. of pure and completely dried sodium chloride is dissolved in water and made up to a volume of one liter in a calibrated flask. This solution contains 1 mg. of sodium per cc.

Magnesium Uranyl Acetate Reagent.—This reagent is prepared in the manner described in a former paper.[1]

Standard Sodium Phosphate Solution.—Thirty-five grams of crystallized disodium hydrogen phosphate is made up to one liter. One cc. of this solution theoretically corresponds to 0.00075 g. of sodium. It should be standardized against measured portions of the standard sodium chloride solution.

Potassium **Ferrocyanide Paper.**—For recognizing the end-point it was found preferable to use potassium ferrocyanide test paper instead of the usual solution, this form giving a sharper end-point. The paper is prepared by immersing large strips of **heavy** white filter paper in fresh 10% potassium ferrocyanide solution and drying them. It keeps indefinitely in a dark bottle.

Procedure.—The precipitation of the sodium and the washing of the precipitate are carried out as directed in the preceding paper.[1] After washing, the suction is continued for two to three minutes in order to remove most of the adhering alcohol. The precipitate and the asbestos felt of the crucible are then transferred to a small beaker, 2–2.5 cc. of glacial acetic acid is added and the precipitate dissolved in 40–50 cc. of hot water, care being taken also to dissolve any precipitate adhering to the sides of the crucible. The solution thus obtained is heated to 90° and titrated at once with the standard sodium phosphate solution, using potassium ferrocyanide test paper as an outside indicator.

Discussion of the Procedure.—For data regarding the allowable limits of other elements that can be present and for manipulative details on this precipitation reference should be made to the former paper.[1]

It is essential to keep the volume of the solution to be titrated down to 50 cc. When quite small amounts of sodium are to be determined it is preferable to use a volume of 25 cc. Experiments demonstrated that the use of larger volumes introduced a two-fold error due to the solubility of the precipitate and the indistinctness of the end-point. The precipitation of uranium as uranyl phosphate is only complete and rapid in hot solution. The maintenance of a temperature of 90° is not so essential at the beginning of the titration but it must be raised to this point or slightly more at the end in order to insure complete precipitation and the attainment of the correct end-point. The end-point of this titration requires some degree of care and practice but with proper precautions there should be no difficulty. Only the clear liquid free from any suspended precipitate of uranyl phosphate should be taken for testing since, as Kolthoff[2] has previously shown,

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[2] I. M. Kolthoff and H. Menzel, "Volumetric Analysis," Vol. II, p. 257. Translated by N. H. Furman, John Wiley and Sons, Inc., New York, 1929.

this precipitate is capable of reacting with potassium ferrocyanide and giving after some seconds the characteristic brown color of uranyl ferrocyanide. For the purpose of rapidly withdrawing one or two drops of clear fluid for testing, the writer has found that a simple filtration pipet[3] is a great convenience. The end-point in this titration is the disappearance of the characteristic brown color when a drop of the filtered liquid is allowed to come in contact with potassium ferrocyanide test paper, but it is essential to allow the same time interval to elapse in each case when observing the result of a test since with very dilute uranium solutions the reaction takes place after different time intervals in accordance with the concentration of uranium in the solution, Attempts were made to use certain phenols, which give characteristic color reactions with uranium, as inside indicators in this titration but all of these color reactions were found to be much less sensitive than the reaction between uranyl salts and potassium ferrocyanide. In general, the best results are obtained if exactly the same procedure is followed for making determinations that is used for standardizing the sodium phosphate solution.

Experimental Results

After devising the above procedure a series of tests was made to determine its value and reliability in actual use. A sodium phosphate solution was first prepared and standardized. Table I shows the values obtained on standardization.

TABLE I

STANDARDIZATION OF THE SODIUM PHOSPHATE SOLUTION

Trial no.	Vol. of standard NaCl soln. used, cc.	Sodium titrated, g.	Volume of standard soln. req., cc.	Value of each cc. of sodium phosphate soln. in terms of sodium, g.
1	20.00	0.0200	27.92	0.000716
2	20 00	.0200	28.00	.000714
3	20.00	.0200	27.90	.000717
4	20.00	.0200	27.97	.000715
5	10.00	.0100	13.95	,000717
6	10.00	.0100	14.00	.000714
			Mean value	0.000715

While the results in the separate experiments in the standardization show a not inconsiderable percentage deviation from the mean value, the absolute differences in terms of grams of sodium are so small that these variations are of no practical consequence within the range covered by the method.

This standardized solution was then used to determine the sodium in known amounts of pure sodium chloride. The results appear in Table II.

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[3] For description *see* E. R. Caley *Ind. Eng. Chem.*, Anal. Ed., 2, 77 (1930).

TABLE II

TEST ANALYSES ON KNOWN AMOUNTS OF PURE SODIUM CHLORIDE

Sodium present, g.	Standard soln. req., cc.	Sodium found, g.	Diff., g.	Sodium present, g.	Standard soln. req., cc.	Sodium found, g.	Diff., g.
0.0250	34.60	0.0247	−0.0003	0.0100	13.95	0.0100	0.0000
.0250	34.73	.0248	− .0002	.0050	7.10	.0051	+ .0001
.0200	27.95	.0200	.0000	.0050	7.00	.0050	.0000
.0200	27.90	.0199	− 0001	.0020	3.00	.0021	+ .0001
.0100	14.03	.0100	.0000	.0020	2.95	.0021	+ .0001
.0100	13.93	.0100	.0000	.0010	1.45	.0010	.0000
.0100	13.95	.0100	.0000	.0010	1.50	.0011	+ .0001
.0100	13.90	.0099	− .0001	.0005	0.90	.0006	+ .0001
.0100	14.00	.0100	.0000	.0005	1.05	.0007	+ .0002

These results were considered to be satisfactory although further experiments showed that the method is not always reliable for amounts below 1.0 mg. due to the influence of the end-point error. The procedure, however, leads to useful results down to 0.5 mg. if care is taken to use only a small volume for titration and to standardize the solution with amounts of sodium approximating those being determined.

A further test of the value of this method was made on samples of various materials containing known amounts of sodium. The results appear in Table III. In the case of the sodium potassium tartrate the purified material was simply dissolved in water and the determination made according to the procedure given. The calcium carbonate was first dissolved in hydrochloric acid and this solution was evaporated nearly to dryness. Then the residue was dissolved in water and the determination made on the latter solution. Standard sample No. 1 of the U. S. Bureau of Standards, stated to contain 0.33% of sodium oxide, was used to test the method on rock material. These samples were decomposed by the J. Lawrence Smith method. The sintered mass was extracted with water as usual and the

TABLE III

THE VOLUMETRIC ESTIMATION OF SODIUM IN VARIOUS SUBSTANCES

Material used	Sample taken, g.	Standard soln. req., cc.	Sodium found, %	Sodium present, %
Crystallized sodium potassium	0.2973	33.70	8.10	8.15"
tartrate	0.2608	29.85	8.18	
"C. p." calcium carbonate	2.0000	4.05	0.14	0.12^{b}
	2.0000	4.25	0.15	
Argillaceous limestone, Bureau	0.5010	2.05^{c}	0.33 (Na_2O)	0.30 (Na_2O)^{b}
of Standards	1.0000	3.70^{c}	0.32 (Na_2O)	0.32 (Na_2O)^{b}
Sample No. 1				0.33 (Na_2O)^{d}

[a] Based on the theoretical composition. [b] Determined by the gravimetric magnesium uranyl acetate method. " This includes the blank on the reagents which amounted to 0 33 cc. This blank was found gravimetrically and then expressed in terms of the titrating solution. [d] According to the U. S. Bureau of Standards.

extract was acidified with hydrochloric acid and evaporated to dryness. The determinations were then made on the water solutions of these residues without removing the calcium. With the exception of the sodium potassium tartrate, the sodium content of each substance was also determined by the gravimetric magnesium uranyl acetate method as a check on the accuracy of the results.

The above results were considered to be-satisfactory evidence of the usefulness of the method. It should be mentioned that these values were obtained in a fraction of the time that would be required to obtain the sodium content of such materials by any of the older methods. This volumetric procedure has certain advantages not possessed even by the gravimetric magnesium uranyl acetate method. There is no need, for example, to free the original solution from insoluble and inert suspended matter when using the volumetric method. The error arising from the determination of sodium in the presence of barium when using a reagent containing considerable sulfate is then eliminated for this same reason. Perhaps the greatest practical advantage of this volumetric procedure lies in the fact that sodium may be determined in the presence of small amounts of phosphates without their preliminary removal before proceeding to the sodium determination.

Summary

A rapid volumetric method for the determination of sodium has been described based upon its precipitation as sodium magnesium uranyl acetate and the titration of the uranium content of the precipitate by means of a standard phosphate solution.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

ADDITION COMPOUNDS OF COPPER HALIDES AND SILVER NITRATE WITH BENZYL SULFIDE[1]

BY EUGENE HARVEY HUBBMAN WITH G. McP. SMITH

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Introduction.—The previously known addition compounds of benzyl sulfide and inorganic metal salts are few in number. Löndahl[2] prepared and analyzed $PtCl_2 \cdot 2(C_7H_7)_2S$, $PtBr_2 \cdot 2(C_7H_7)_2S$, $PtI_2 \cdot 2(C_7H_7)_2S$, $Pt(OH)NO_2 \cdot 2(C_7H_7)_2S$, $Pt(NO_2)_2 \cdot 2(C_7H_7)_2S$ and $PtCl_4 \cdot 2(C_7H_7)_2S$. Herrmann[3] obtained two compounds of the composition $AuCl_2 \cdot (C_7H_7)_2S$ and $AuCl \cdot (C_7H_7)_2S$, and Smith[4] prepared the gold halide compounds $AuBr_2 \cdot (C_7H_7)_2S$,

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[1] Thesis presented to the Graduate School of the University of Washington, in partial fulfilment of the requirements for the degree of Master of Science.

[2] H. Löndahl, J. *prakt. Chem.*, [2] 38, 521 (1888).

[3] F. Herrmann, *Ber.*, 38, 2813 (1905).

[4] G. McP. Smith, THIS JOURNAL, 44, 1769 (1922).

$AuBr\cdot(C_7H_7)_2S$, $AuI_2\cdot(C_7H_7)_2S$ and $AuClI\cdot(C_7H_7)S$. Also, Forster, Cooper and Yarrow[5] obtained from ferric chloride and benzyl sulfide, in ether, a product that proved to be $FeCl_2\cdot(C_7H_7)_2S$.

The purpose of this study was to prepare and study similar compounds with copper and silver halides, silver nitrate and salts of cadmium.

A. Copper Halides.—Since cupric chloride and bromide, and cuprous chloride, bromide and iodide were all found to yield compounds of the type $CuX\cdot 2S(C_7H_7)_2$, it will suffice to describe a general method for their preparation.

The copper halide was mixed with benzyl sulfide[6] in the proportion of $1CuX_2$ to $4(C_7H_7)_2S$, or $1Cu_2X_2$ to $8(C_7H_7)_2S$, and the mixture dissolved in the least possible amount of gently boiling acetone. In the case of the cupric salts, either in acetone or alcohol, the solutions rapidly faded in color with the evolution of a sharp penetrating odor, due to the oxidation of benzyl sulfide to the sulfoxide, by the cupric halide, as previously noted by Herrmann[3] in the case of gold chloride. In the case of a cuprous salt it was necessary to allow the mixture to stand overnight in acetone in order to complete the reaction. In all cases a portion of the product usually separated in the form of lustrous fine white needles, but upon the addition of a little more acetone and warming, these redissolved and the solution could be decanted or filtered from a small amount of sludge. The needles were then crystallized from the acetone solution, usually by partial evaporation and cooling. They were washed with a very little cold acetone and dried between layers of filter paper. Upon analysis they were found to be of the type $CuX\cdot 2S(C_7H_7)_2$.

The $CuCl\cdot 2S(C_7H_7)_2$ melts at 98.3° and decomposes about a degree higher, the $CuBr\cdot 2S(C_7H_7)_2$ melts at 87.5–87.8°, and the $CuI\cdot 2S(C_7H_7)_2$ melts at 63.5°.

Upon redissolving these compounds in either acetone or alcohol, the separation in small quantity of an insoluble white or cream-colored substance was noted, which upon analysis was found to consist of the corresponding cuprous halide. For this reason the addition compounds are best recrystallized from small amounts of the solvent, in the presence of a small quantity of benzyl sulfide. In this way the dissociation may be prevented.

All three of these compounds are insoluble in water. Dissolved in acetone, in the presence of sufficient benzyl sulfide to prevent the precipitation of cuprous halide, they were found to yield precipitates with hydrogen sulfide but only a fraction of the copper could be thus precipitated.

For analysis, the addition compounds were best decomposed by the oxi-

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[5] Forster, Cooper and Yarrow, J. Chem. *Soc.*, 111, 809 (1917).

[6] The benzyl sulfide was prepared from alcoholic solutions of potassium sulfide and benzyl chloride, according to Marcker [Ann., 136, 88 (1865)]. The product was purified by recrystallization from alcohol.

dation of a small weighed sample in a porcelain casserole with concentrated sulfuric and nitric acids; but it was found necessary alternately to concentrate the sulfuric acid by evaporation and to add the nitric acid from ten to fifteen times. The resulting cupric sulfate was treated with potassium iodide and the liberated iodine titrated with standard sodium thiosulfate solution.

TABLE I

ANALYTICAL DATA

No.	From	Sample, g.	$Na_2S_2O_3$ soln., g.[a]	Cu in sample, g.	Calcd. % of copper in
1	Cupric chloride	0.2130	4.15	12.11	$CuCl\cdot 2(C_7H_7)_2S$
1	Cuprous chloride	.2907	5.60	11.97	12.05
2	Cupric bromide	.2563	4.58	11.11	$CuBr\cdot 2(C_7H_7)_2S$
2	Cuprous bromide	.3358	5.97	11.05	11.11
3	Cuprous iodide 1	.2108	3.44	10.14	$CuI\cdot 2(C_7H_7)_2S$
3	Cuprous iodide 2	.1315	2.21	10.44	10.21

[a] Copper equivalent of $Na_2S_2O_3$ solution, 0.006216 g. per cc.

B. Silver Nitrate.—In attempting to prepare addition compounds of silver halides with benzyl sulfide in a manner similar to that used by Sheppard and Hudson[7] with silver halides and thiosinamine, mixtures of benzyl sulfide and potassium chloride, bromide and iodide, respectively, were put in alcohol and an alcoholic solution of silver nitrate added to each. The proportions were $1AgNO_3$ to $1KX + 4(C_7H_7)_2S$. The mixtures were allowed to stand overnight and were found to have yielded a compact, pasty white solid on the bottom of the beaker. The precipitates so formed were washed by decantation with alcohol to dissolve any excess benzyl sulfide and then with water to remove any excess potassium salt. On drying between filter papers, each precipitate constituted a white powder melting at 105.5°, showing that the product from each solution was the same—evidently from the silver nitrate and the benzyl sulfide present in each case. For this reason silver nitrate and benzyl sulfide were then mixed in the proportions of $1AgNO_3$ to $4(C_7H_7)_2S$ and dissolved in alcohol. After standing overnight, a white pasty solid was present. This was washed with small amounts of alcohol and dried between filter papers, yielding a white powder which also melted at 105.5°. This confirmed the conclusion previously drawn that the reaction was between benzyl sulfide and the silver nitrate. This substance could not be recrystallized from alcohol, because brown metallic silver separated as the solid went into solution. It was therefore, quickly washed with small amounts of cold alcohol and dried between filter papers.

The addition compound of silver nitrate and benzyl sulfide was analyzed by simply igniting the sample in porcelain over a Bunsen flame and weighing the residue of silver. A very small flame was used at first, in order to

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[7] Sheppard and Hudson, THIS JOURNAL, 49,1814 (1927).

prevent spattering, but after the sample had thoroughly charred and was no longer liquid, the flame was turned on full with plenty of air to accomplish oxidation.

Anal. Subs., 0.1306: _Ag,_ 0.0237. Calcd. for $AgNO_3 \cdot 2(C_7H_7)_2S$: Ag, 18.28. Found: Ag, 18.15.

C. Other Attempts.—Besides the unsuccessful attempts to prepare addition compounds of benzyl sulfide and silver halides, referred to in the above, attempts were also made to prepare them directly from the silver halides and benzyl sulfide, in the presence of alcohol. The results were negative.

Each of the cadmium halides was also mixed with benzyl sulfide in varying proportions and dissolved in alcohol and in acetone, but in no instance was a new product obtained.

Summary

1. The following new addition compounds of cuprous halides and silver nitrate with benzyl sulfide have been prepared and described: $CuCl \cdot 2(C_7H_7)_2S$, $CuBr \cdot 2(C_7H_7)_2S$, $CuI \cdot 2(C_7H_7)_2S$ and $AgNO_3 \cdot 2(C_7H_7)_2S$.

2. The addition compounds of cuprous halides with benzyl sulfide in alcohol or acetone solution have been shown to be in equilibrium with benzyl sulfide and the cuprous halide as indicated by the equation

$$CuX \cdot 2(C_7H_7)_2S, \rightleftharpoons CuX + 2(C_7H_7)_2S$$

3. Similar attempts to prepare addition compounds of benzyl sulfide with silver halides and with cadmium halides met with failure.

SEATTLE, WASHINGTON

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

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. IX. THE ELECTRIC MOMENTS OF CERTAIN SUBSTITUTED PHENOLS AND THEIR RELATION TO THE STEREOCHEMISTRY OF THE OXYGEN ATOM

BY JOHN WARREN WILLIAMS AND JOHN M. FOGELBERG

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Introduction

Studies of electric moment data are beginning to give considerable information concerning the structure of molecules. It has, for example, been quite definitely established that the four valences of the carbon atom are directed toward the corners of a regular tetrahedron.[1,2] The structures of the simple polar molecules, water and ammonia, as deduced from infra-red

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[1] **(a) Williams, _Physik._ Z., 29, 683 (1928); (b) _Z. physik. Chem.,_ 138A, 75 (1928); (c) _Chemical Reviews,_ 6, 589 (1929).**

[2] **Höjendahl, "Studies of Dipole Moment," Dissertation, Copenhagen, 1928.**

absorption spectra,[3] seem to be in agreement with the conclusions which have to be drawn from electric moment studies. These configurations have been at least partially substantiated in the case of the oxygen atom by electric moment data of one of us,[1,4] and appear to be substantiated in the case of the nitrogen atom by the electric moment data for the substitution products of ammonia which have been calculated by Höjendahl[2] from dielectric constant data of Pohrt.[5] However, it is only fair to say that these latter data must be used with caution, since they are, in every case where a comparison is possible, only in approximate agreement with the results of the more recent measurements undertaken solely for the purpose of the calculation of the electric moment. In addition, one would have to conclude from them that the polarity of a molecule was dependent on the length of the hydrocarbon chain, although the contrary has been proved in the case of the alcohols[6] and ketones.[7] It is the purpose of this article to present electric moment data for a number of substituted phenols and to discuss their significance, particularly from the standpoint of the stereochemistry of the oxygen atom.

Experimental Data

The electric moments of the several molecules have been obtained by the method of the binary mixture, completely described in the previous papers of this series.[8] All dielectric constant and density determinations were made at 25°. All chemicals used were subjected to rigorous purifications. In short, every precaution for precision measurements was taken. The method of measurement of the dielectric constants was that now used by a number of investigators.[9] A frequency of 10^6 cycles was used.

The dielectric constant and density data for the various binary mixtures are presented in Table I. In this table f_1 is mole fraction of the solvent, benzene; d_4^{25} is density of the solution; ϵ is its dielectric constant; $P_{1,2}$ is molar polarization of the solution $= \left(\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{f_1M_1 + f_2M_2}{d} = f_1P_1 + f_2P_2\right)$ and P_2 is molar polarization of the solute molecule, that is, the molecule whose electric moment is being determined. The quantity $f_1M_1 + f_2M_2$ is a fictitious molecular weight of the solution, being made up of the mole

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[3] Eucken, Z. *Elektrochem.*, 26,377 (1920); Heisenberg, Z. *Physik*, 26, 196 (1924); Hund, *ibid.*, **31**, 81 (1925); 32, 1 (1925); Debye, "Polar Molecules," Chemical Catalog Co., New York, 1929, Chapter IV; Barker, *Phys. Rev.*, 33,684 (1929); Badger and Cartwright, *ibid.*, 33, 692 (1929).

[4] Williams, *Physik.* Z., 29, 271 (1928).

[5] Pohrt, Ann. *Physik*, 42, 569 (1913).

[6] Mahanti and Das Gupta, *Ind.* **J.** *Physics*, 3,467 (1929).

[7] Wolf and Lederle, *Physik.* *Z.*, 29, 948 (1928).

[8] For a discussion of the method, and of the assumptions and approximations which must be made in its use, see Williams and Krchma, THIS JOURNAL, 49,1676 (1927).

[9] See Sack, *Ergebn. d. exakt. Naturwiss.*, VIII, 307 (1929).

fraction of the solvent times its molecular weight plus the mole fraction of the solute times its molecular weight.

From the molar polarization of the solute molecules the respective electric moments have been calculated. The results of these calculations are given in Table II. As in Table I, the symbols used are exactly those of the previous articles; they are, however, included to assist the reader. The quantity P''_2 is that part of the total polarization of the solute molecule

TABLE I

DIELECTRIC CONSTANT AND DENSITY DATA FOR SUBSTITUTED PHENOLS

o-Chlorophenol

Purified by fractional distillation under reduced pressure. B. p 52–54' at 7 mm

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1.000	0.8735	2276	2666	75
0.9986	,8741	2 280	26 73	74
.9958	.8754	2 288	26 85	73
9931	8765	2 295	26 97	71 5
.9890	.8785	2 304	27 11	67 6
.9796	.8827	2 328	27 49	67 6
.9664	.8888	2 371	28 13	70 5

m-Chlorophenol

Purified by distillation under reduced pressure M. p. 31–32'

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1 000	0 8735	2 276	26 66	130
0 9986	8741	2 286	26 81	136
9944	8759	2 314	27.24	130
9903	8778	2 343	27 67	130
9864	8798	2 371	28 07	130
9796	8827	2 418	28 75	129
.9730	.8859	2 463	29 38	128

p-Chlorophenol

Purified by fractional distillation under reduced pressure. M. p. 40–41°

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1 000	0 8735	2 276	26 66	180
0.9986	.8741	2 289	26 86	170
9958	.8751	2.314	27 24	164
.9931	.8764	2 331	27 49	148
.9890	.8783	2 364	27 97	146
.9796	.8826	2.435	29 00	141
.9664	.8888	2 545	30 50	141

o-Nitrophenol

Purified by distillation under reduced pressure. M p. 44–45°

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1 000	0 8735	2 276	26 66	235
0 9987	8742	2 294	26 93	235
.9962	8755	2 330	27 47	237
.9936	8768	2 366	27 99	235
.9898	8788	2 415	28 69	226
9809	8834	2 547	30 51	228
9689	8897	2 718	32 72	222

m-Nitrophenol

Purified by recrystallization from benzene M. p. 96–97''

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1.000	0 8735	2 276	26 66	345
0.9987	.8742	2 303	27 06	335
,9962	.8756	2 362	27 92	364
,9936	.8771	2 418	28 71	346
9898	.8792	2 509	29 95	349
,9861	8808	2 591	31 04	345

p-Nitrophenol

Purified by recrystallization from benzene. M. p. 113–114°

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1 000	0 8735	2 276	26 66	563
0 9987	8743	2 324	27 36	567
9974	.8750	2 369	28 01	555
9962	8758	2 419	28 74	574
9936	.8773	2 520	30 07	559

o-Bromophenol

Purified by fractional distillation. B. p. 189–191° (742 mm.)

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1.000	0 8735	2 276	26 66	74
0.9990	8744	2 280	26 73	
,9969	,8762	2 285	26 81	74
.9948	,8781	2 291	26 92	76
.9918	.8807	2 300	27 05	74
.9867	8852	2 314	27 29	74
.9798	.8913	2.332	27 59	73

p-Bromophenol

Purified by fractional distillation under reduced pressure. M p. 64–65°

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1 000	0 8735	2 276	26 66	206
0 9990	8744	2 287	26 84	194
9969	8763	2 304	27 09	166
9948	8783	2 318	27 30	151
9978	8811	2 342	27 65	147
9867	8863	2 386	28 20	148
9798	.8940	2 440	29 01	143

TABLE I (Concluded)

o-Anisidine[a]
B. p. 219–221° (742 mm.)

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1.000	0.8735	2.276	26.66	83
0.9985	.8739	2.281	26 74	82
.9957	.8747	2.290	26.91	83
.9928	.8755	2.299	27.05	80
.9885	.8767	2.312	27.26	79
.9829	.8782	2 330	27.56	79

p-Anisidine[a]
M. p. 56–58"

f_1		ϵ	$P_{1,2}$	P_2
1.000	0 8735	2.276	26.66	104
0.9985	.8739	2.283	26.78	106
.9957	8748	2.296	26 99	104
.9928	.8755	2 310	27.21	102
.9885	.8769	2.331	27.54	103
.9829	.8786	2.360	27.98	104

m-Aminophenol
Purified by recrystallization from toluene. M. p. 123–124°

f_1	d_4^{25}	ϵ	$P_{1,2}$	P_2
1.000	0.87354	2.276	26 66	101
0.99837	.87410	2.284	26.78	101

[a] The authors are indebted to Mr. C. F. Koelsch of our Division of Organic Chemistry for the preparation and purification of these compounds.

TABLE II
ELECTRIC MOMENT DATA FOR SUBSTITUTED PHENOLS

Molecule	P_2	P_2''	P_2'	$\mu \times 10^{18}$
o-C_6H_4OHCl	75	33	42	1.43
m-C_6H_4OHCl	130	33	97	2 17
p-C_6H_4OHCl	180	33	147	2.68
o-$NO_2C_6H_4OH$	235	33	202	3.10
m-$NO_2C_6H_4OH$	348	33	315	3.90
p-$NO_2C_6H_4OH$	563	33	530	5.05
o-BrC_6H_4OH	74	36	38	1.36
p-BrC_6H_4OH	206	36	170	2.86
o-$NH_2C_6H_4OCH_3$	83	37	46	1.50
p-$NH_2C_6H_4OCH_3$	104	37	67	1.80
m-$NH_2C_6H_4OH$	101	32	69	1.83"

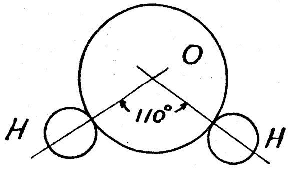
[a] This value was obtained from a single measurement in a very dilute solution and may, therefore, be subject to appreciable error.

caused by the deformation of the molecule, and is given by the quantity $\left(\frac{n_D^2 - 1}{n_D^2 + 2} \cdot \frac{M_2}{d}\right)$, (where n_D is refractive index for the "D" line at 25°); P_2' is that part of the total polarization of the solute molecule caused by its actual orientation in the field and is given by the quantity $\left(\frac{4\pi}{3} N \frac{\mu^2}{3kT}\right)$, where μ is the electric moment of the molecule and the remaining factors are constants.

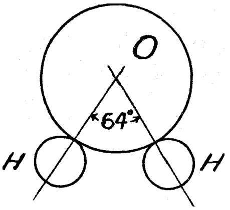
Discussion

There is now available ample evidence that an electric moment may be considered a characteristic property of a polar group. It is, in addition, a vector quantity, and as such there can be assigned to it both a magnitude and a direction, that is, an electrical character. For the latter purpose it is necessary arbitrarily to assign an electrical character to some one group. In the previous article of this series[10] it was possible to assign such a character to eight atoms or groups of atoms, making the simple assumption that the CH_3 group was positive. Included in a table presented in that article a negative character was assigned to the OH and OCH_3 groups, and it was the only character which could be assigned to these groups with the data available at that time. Shortly afterward it was found by one of us[11] that *p*-chlorophenol had a much larger electric moment than o-chlorophenol, indicating that in these particular compounds the OH group apparently was behaving as a positive rather than as a negative group, since there can be no question concerning the negative character of the chlorine atom. The manner in which these polarities have been assigned has been discussed in previous articles.[1,2,10] The assumptions underlying this treatment have been previously discussed and will not be repeated here. This method of assigning an electrical character to an atom or group is wholly satisfactory provided the group is simple in nature, but when the group which is substituted has attained any degree of complexity it may lead to difficulty for two reasons. (1) There may be an interaction between the groups. (2) It may be necessary to take into account the stereochemistry of the particular atom of the substituent group which is attached to the benzene (or other hydrocarbon) residue. Both of these factors have been previously recognized and described by one of us[4] and also independently by Höjendahl,[2] and subsequent work has only served to strengthen these conclusions, except that as the complexity of the molecule in question becomes greater, it is becoming increasingly difficult to separate these two effects.

In this article the second of these two factors is involved, since an oxygen atom is attached directly to the benzene nucleus. It is necessary first to consider the structure of the water molecule. An excellent summary of the available material has recently been given by Debye.[12] It is concluded that there are two possible models, both triangular in form, and, from the calculations given, the acute model is considered to be the more probable. The two possible models are reproduced below.



A



B

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[10] Williams, THIS JOURNAL, 50,2350 (1928).

[11] Williams, *Physik. Z.*, 29, 683 (1928).

Debye, "Polar Molecules," The Chemical Catalog Co., New York, 1929.

It has already been suggested[1,4] that diethyl ether, methyl alcohol, anisole, the cresols, derivatives of the dihydroxybenzenes and other like oxygen derivatives are built up of structural oxygen units, differing only in the complexity of the group attached to the force fields ordinarily referred to as the valence bonds. In other words, all these compounds have structures similar to those given above for the water molecule. Such a structure, for example, appears to give the only adequate explanation for the fact that hydroquinone diethyl ether has a finite dipole moment.[4] In order to account for the electric moments of the substituted phenols given in Table II of this article, it is necessary as well to assume that they are derivatives of oxygen, rather than of benzene.

To predict the exact electric moment of molecules having such structures will not be an easy problem. The main difficulties appear to be: (1) the angle between the directions of the two valences of the oxygen atom is as yet uncertain and unobtainable. It is usually assumed to be 110°;[13] however, all that can be said with certainty is that it is less than 180°. Furthermore, there is every reason to believe that with two substituents on the same carbon atom they will either mutually repel each other if they are charged alike or will mutually attract each other if they are not charged alike. Very definite proof of such a mutual repulsion has been given for the case of two and three chlorine atoms attached to a single carbon atom,[14] and in this same article it is shown that like atoms or groups attached to adjacent carbon atoms mutually repel each other. Furthermore, it appears that this repulsion may even be exerted over a distance equivalent to four carbon atoms.

(2) In the case of the ortho and meta compounds it has been assumed by other investigators that there is free rotation of the benzene nucleus (with its substituted group) about the valence bond or shared electron pair. In any calculation which is made it will then be necessary to assign an equal probability to all possible positions about the circumference of the vector projected in a plane for the calculation. Such a procedure will limit the accuracy of any calculation, since it is very doubtful whether all possible positions of the rotation are equally probable under these circumstances.

The second difficulty in the calculation of the electric moment of an oxygen derivative does not apply in the case of a para-disubstituted hydroxy derivative of benzene. Thus Wolf[13] has been able to calculate the moments of *p*-cresol, *p*-cresyl methyl ether and *p*-chlorophenol with a reasonable degree of accuracy, making the assumptions that the OH is positive and that the angle between the two vectors characteristic of the two groups is always 110°.

Thus it appears desirable to consider molecules of the type under dis-

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[13] Wolf, *Z. physik.* **Chem.,** 3B, **128 (1929); Eucken and Meyer,** *Physik. Z.,* **30, 397 (1929).**

[14] Williams, Z. *physik. Chem.,* **138A,** 75 **(1928).**

cussion in this article as being built about an oxygen atom with its two valence bonds making an angle considerably less than 180° to each other, and to avoid assigning either a positive or a negative character to either the OH group or the OCH_3 group. Unpublished data of the authors for substituted anilines show that exactly similar difficulties are encountered in the case of the NH_2 group,[15] and that the electric moment data are most readily explained by considering these compounds to be derivatives of the ammonia molecule whose structure has been referred to in the introduction. These considerations are admittedly qualitative in character because one cannot as yet determine with any degree of security the magnitude of the angle which the various vectors make with each other.

The data of this article further emphasize the fact that equations such as those of Thomson[16] to calculate the electric moment of disubstitution products of benzene can be of use only in the case of substituent atoms or very simple substituent groups. If such atoms as carbon, oxygen and nitrogen are attached to the ring, a three-dimensional vector diagram must be considered because the valences of these atoms are directed in space rather than in a plane, so that when and only when the angles between these valence bonds become known with a reasonable degree of certainty will it be possible to calculate the electric moments of this type of molecule. In addition this calculation will be correct only when there is no interaction between the groups themselves, or when any such interaction between groups may be quantitatively accounted for. At present it appears that this interaction between groups is also of great significance.

Eucken and Meyer[17] have recently made the suggestion that in vectorial considerations of this sort it would be better to use values characteristic of linkages between atoms rather than to assign values to the atoms or groups of atoms themselves. One may at least maintain that such values are of no greater utility than the old ones, because they are calculated rather than observed by a direct experiment, and therefore involve questionable assumptions. This is particularly noticeable in the case of the values reported for the H—O and C—O linkages, both of which depend on an assumed angle between the two valence bonds of the oxygen. The electric moment for *p*-chlorophenol is calculated to be $\mu = 2.3$ X 10^{-18} e. s. u. We have been extremely careful with the determination of the electric moment of this molecule and find a value, $\mu = 2.68$ X 10^{-18} e. s. u. A value reported previously by one of us,''' p = 2.4 X 10^{-18} e. s. u., was found to have been slightly low because the dielectric constant and density data were not obtained for solutions containing less than 0.006 mole per cent. of *p*-chlorophenol in benzene solution.

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[15] These data will be presented in a later communication.

[16] Thomson, *Phil.* Mag., 46, **513** (1923).

[17] Eucken and Meyer, *Physik. Z.*, **30, 397** (1929).

Summary

1. Electric moment data for a number of substituted phenols have been obtained by the method of the binary mixture. The dielectric constant and density data have been included.

2. The data have been discussed from the point of view of the stereochemistry of the oxygen atom.

3. It is shown that the dipole moment of a molecule can in general be calculated only provided the vectors characteristic of the groups be considered to be acting in space, for two reasons: (a) it is necessary to take into account the stereochemistry of the atoms forming the substituent group, and (b) it is necessary to take into account mutual attractions or repulsions between substituent groups unless they be separated by at least a distance equivalent to a chain of four carbon atoms, that is, by 5 Å.

4. Our knowledge is not at present sufficient to enable us to calculate with any degree of accuracy the electric moment of an "oxygen derivative."

MADISON, WISCONSIN

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

THE COMPRESSIBILITY ISOTHERMS OF HYDROGEN, NITROGEN AND A 3:1 MIXTURE OF THESE GASES AT TEMPERATURES OF –70, –50, –25 AND 20° AND AT PRESSURES TO 1000 ATMOSPHERES

BY EDWARD P. BARTLETT, HARRY C. HETHERINGTON, HAMLINE M. KVALNES AND THOMAS H. TREMEARNE

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This investigation was undertaken to provide data supplementing the earlier results obtained in this Laboratory on the compressibility of hydrogen, nitrogen and a 3 : 1 mixture of these gases at temperatures between 0 and 400° and at pressures to 1000 atmospheres.[1] The new data cover the temperature range –70 to 20°. They should be useful in the design of condenser equipment for synthetic ammonia plants and should be of especial interest in the study of equations of state for real gases.

Compressibility data id this temperature range dealing with hydrogen and nitrogen are already available.[1,2] However, at temperatures below 0°

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[1] Bartlett, Cupples and Tremearne, THIS JOURNAL, 50, 1275 (1928).

[2] (a) Natterer, *Pogg. Ann. Physik. Chem.*, *94*, *436* (1855); (b) Amagat, *Ann. chim. phys.*, [6] **29**, 68 (1893); (c) Witkowski, *Krakauer Anzeiger*, 305 (1905); (d) Kohnstamm and Walstra, *Proc. Roy. Acad. (Amsterdam)*, 19, 203 (1914); (e) Schalkwijk, *Comm. Phys. Lab. Univ. Leiden*, No. 70; (f) Onnes, Crommelin and Smid, *ibid.*, No. 146b; (g) Holborn and Shultzer, *Ann. Physik*, 47, 1089 (1915); (h) Smith and Taylor, THIS JOURNAL, 45, 2107 (1923); (i) Smith and Taylor, *ibid.*, 48, 3122 (1926); (j) Onnes and Penning, *Arch. Neerland. sci.*, IIIA, *6*, 277 (1923); (k) Crommelin and Swallow, Comm. *Phys. Lab. Univ. Leiden*, *No.* 172a (1924); (l) Onnes and van Urk, *ibid.*, No. 169d

investigations have been limited to pressures under 100 atmospheres. At 20° there have been reported only the data on hydrogen by Kohnstamm and Walstra at pressures to 1000 atmospheres, the data of Schalkwijk on hydrogen at pressures to 60 atmospheres, the data by Onnes, Crommelin and Smid on this same gas at pressures to 100 atmospheres, and the data by Verschoyle on hydrogen, nitrogen and their mixtures at pressures to 200 atmospheres. In the vicinity of 20° are to be found Amagat's data at 15–16° on both gases at pressures to 1000 atmospheres, Scott's data on hydrogen at pressures to 170 atmospheres and at 25°, and Bartlett's data on the 3:1 mixture of hydrogen and nitrogen at pressures to 1000 atmospheres and at 25°. At 0 and 50° extensive investigations on both gases have been conducted. The new results presented in this report will serve to round out the data at 20°.

Method.—As in previous work a quantity of gas at known pressure and temperature is confined in a heavy metal pipet of known capacity. The gas is allowed to expand into a gas buret maintained at constant temperature and the quantity of gas determined by measurement of a fixed volume at a measured pressure, not far above or below atmospheric pressure.

Preparation and Purification of the Gases.—The hydrogen was prepared by the electrolysis of a solution of sodiym hydroxide. Analyses by a low pressure analytical method devised by Kvalnes[3] indicated a possible maximum nitrogen impurity of 0.06–0.09%. The nitrogen was a commercial product manufactured by the air liquefaction process. Analysis by a method devised by Leatherman and Bartlett[4] indicated a maximum inert gas content of 0.06–0.08%. No oxygen could be detected by the usual method of analysis. However, any traces of this gas were removed on finely divided copper (reduced copper oxide) under pressure at 400°. The 3:1 mixture of hydrogen and nitrogen was made by "cracking" pure anhydrous ammonia on a rugged ammonia catalyst at dull red heat. An analysis of the resulting gas showed 74.6 ± 0.1% of hydrogen and 25.4 ± 0.1% of nitrogen by volume. Both the hydrogen and the 3:1 mixture were purified under pressure from any possible traces of oxygen by passage over finely divided copper at 325°. All of the gases were subsequently dried by passage through a trap maintained at 0° with a mixture of ice and water and a second trap maintained at about −80° by means of a mixture of solid carbon dioxide and acetone.

Apparatus.—The apparatus used in this investigation has been described in an earlier report from this Laboratory.[5] For work at low temperatures it has been found expedient to shorten the head and valve stems of the two-valve high-pressure pipet and

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(1924); (m) Holborn and Otto, *Z. Physik*, **33**, 1 (1925); (n) Holborn and Otto, *ibid.*, 38, 359 (1926); (o) Verschoyle, Proc. Roy. *Soc.* (London), **111A**, 552 (1926); (p) Bartlett, THIS JOURNAL, 49, 687 (1927); (q) Bartlett, *ibid.*, 49, 1955 (1927); (r) Scott, Proc. Roy. *Soc.* (London), **125A**, 330 (1929).

[3] A description of this method will eventually appear in a separate report.

[4] Leatherman and Bartlett, Ind. Eng. *Chem.*, Analytical Edition, 1, 223 (1929).

[5] For a diagrammatic drawing and description of the compression and purification systems, see Bartlett, THIS JOURNAL, 49, 68 (1927). For description of the general arrangement of the expansion and measuring devices see Bartlett, Refs. 1 and 2. For description of the high pressure pipet see Bartlett, Cupples and Tremearne, Ref. 1.

to omit the heating unit and water-cooling system described in the earlier report. The pipet was of copper alloy instead of the steel hitherto used. The pipet bath was designed especially for maintaining temperatures between 0 and —70° to within ±0.03°. Because of its unique yet simple construction a somewhat detailed description of this apparatus is presented.

A sectional diagram of the thermostat is given in Fig. 1. For simplicity of construction A and B are separate units. The boxes are ruggedly constructed of 1-inch lumber. The copper cans E are of 22-gage copper brazed to form one-piece water-tight units. These fit over the edges of the containing boxes and are nailed in place. The insulation material D is ground cork. Each unit is 30 cm. wide; the other dimensions are given in the figure.

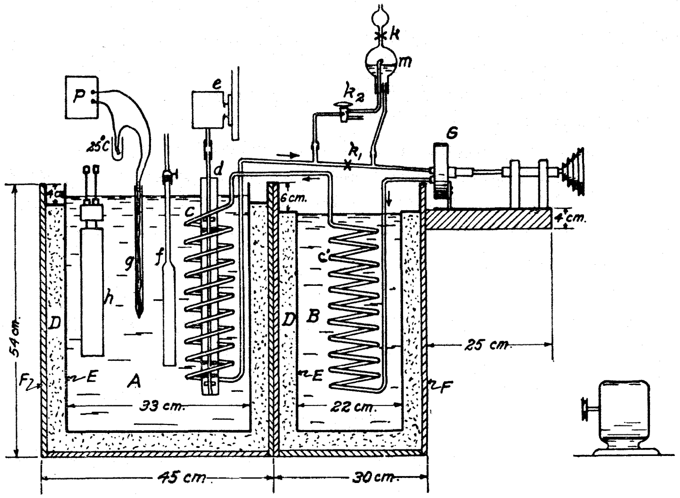

Fig. 1.—A low temperature thermostat.

The coils C, C′ and connections to the pump G are of 0.63-cm. copper tubing, each coil being about 3 meters in length. Acetone is used in the coil system. The rate of flow is determined by the proper choice of the pulley used on the shaft of the pump and by the proper adjustment of the stopcocks k_1 and k_2. The by-pass through the 500-cc. flask m is for the purpose of adding acetone and for observing the rate of flow. The pump was designed and built at this Laboratory; however, any of the regular water-circulating pumps should prove satisfactory.

Unit **A,** in which the temperature is maintained constant, contains a stirrer d driven by an overhead motor, an immersion knife heater f, a copper–constantan thermocouple g, and the high pressure pipet h. The bath liquid is acetone, which is kept in vigorous agitation. The heater is operated from a remote control switch located conveniently near the potentiometer by which the temperature of the bath is determined.

To operate the thermostat, unit B is filled with a mixture of solid carbon dioxide and acetone, while the acetone in unit A is brought to approximately the desired temperature by adding solid carbon dioxide. The rate of flow of acetone through the coils is adjusted until the liquid in A tends toward a temperature slightly below that desired. The operator at the potentiometer then regulates the current through the knife heater to maintain the temperature constant. When the acetone in **A** is comparatively dry and vigorously agitated, very little attention is needed for accurate control of temperature, once the proper flow of acetone in the coils is attained.

The acetone rapidly condenses water from the atmosphere at temperatures below 0°, and at −70° in a humid atmosphere will condense enough water in four or five days to render the mixture too viscous for adequate stirring. When this condition is evidenced by fluctuations in the potentiometer readings a new supply of dry acetone is placed in the thermostat.

The thermostat arrangement described possesses a flexibility that is highly advantageous when the apparatus in the thermostat is of a fixed nature and it is desired to work at two or more temperatures within a short period of time. A twenty-five degree change in temperature is effected in from ten to twenty minutes, while a fifty degree change is made in from twenty to thirty minutes, providing the temperature is not below −50°. A somewhat longer time proportionately is required to lower the temperature from −50 to −70°.

Calibration.—All volume, temperature and pressure measuring devices employed in this investigation were carefully calibrated. The low temperatures were measured by means of a copper–constantan thermocouple calibrated at 100, 50, 25, 0 and −25° against standard thermometers.

Pipet calibrations were carried out by the methods described in earlier reports.[5] The measurements to 150 atmospheres were, in general, made in a pipet of 20-cc. capacity. At this pressure a direct comparison of size was made at each temperature with a pipet of about 4.1-cc. capacity and the *PV* measurements at higher pressures were conducted with the smaller pipet.

The effect of temperature and pressure on the pipet volume depends upon the physical properties of the metal used. Analysis showed the copper alloy pipets to be of the following composition

Copper	65.00%	Iron	2.60%	Manganese	5.03%
Zinc	21.69%	Aluminum	5.72%	Lead	(Trace)

The Bureau of Standards[6] reports the ultimate tensile strength of a single sample of this material to be 129,000 pounds per sq. inch and Young's Modulus (E) to be approximately 16,000,000 pounds per sq. inch. The linear coefficient of thermal expansion determined by the interferometer is 1.90×10^{-5} from −51 to 20° and 1.97×10^{-5} from 20 to 263°.[7] The elongation under load is known to be so small at the temperature used in this investigation that its effect may be neglected.

Love's formula[8]

$$\Delta V = \frac{V_0}{E(r_2^2 - r_1^2)}\, 3(1 - 2\mu)(P_1r_1^2 - P_2r_2^2) + 2(1 + \mu)(P_1 - P_2)r_2^2$$

was employed to determine change in volume ΔV with change in total pressure $(P_1 - P_2)$. r_1 and r_2 are the internal and external radii of the pipet and P_1 and P_2 are the internal and external pressures.[9] The value

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[6] Courtesy of L. B. Tuckerman, Bureau of Standards.

[7] Courtesy of G. W. Merritt, Bureau of Standards.

[8] Love, "Mathematical Theory of Elasticity," Cambridge University Press, 1920, p. 141.

[9] It has been called to the attention of one of the authors that in his earlier papers he has incorrectly defined P_1 and P_2. This was an oversight in proof-reading. It does not affect the accuracy of data presented in these papers. See THIS JOURNAL, 49, 691 (1927), and 50, 1277 (1928).

of Poisson's ratio μ for this alloy is still under investigation but it is believed to be approximately 0.30, and this value was used in the calculations. Supporting evidence for this value of μ has been independently and subsequently procured. First a pipet was calibrated with hydrogen at 100 and at 800 atmospheres and its size at the two pressures calculated by the use of P V data for hydrogen which had been determined in a steel pipet. The actual change in volume between these pressures amounted to 0.19%, while that calculated by the formula was 0.17%. In a similar manner the pipet was calibrated with nitrogen at 200 and at 1000 atmospheres. The observed change in volume was 0.20% and the calculated change 0.19%. This agreement is well within the limit of accuracy of the experimental work.

In the calculation of change in volume of the pipet with change in temperature it was assumed that the average cubical coefficient of expansion is three times the average linear coefficient of expansion of the metal for the same temperature range.[10] Data for more refined calculation of the magnitude of this change are not available. However, it is known that when a calculation of this type is made for steel, the difference between volume changes calculated by this simple method and by the use of an equation of the type[11]

$$V_t = V_0 (1 + at + bt^2 - ct^3)$$

differ by so little as to be well within the limits of accuracy of the present experimental work.

Experimental Results

The data obtained in this investigation are presented in the form of Amagat units, that is, the unit gas mass is the mass of 1 liter at 1 atmosphere pressure and 0°. At this pressure and temperature P V is unity.

In addition to the new data the tables also include results obtained by other investigators in so far as they cover approximately the same pressure and temperature ranges. Interpolations and short extrapolations have been necessary in some cases to make these scattered data strictly comparable. This is especially true in calculating Holborn's P V data at 20, -25 and $-70°$ from his observed data at 50, 0, -50 and $-100°$; and in calculating Amagat's data at 20° from his observed results at 0 and 15–16°. Where the PV–T relationships are not approximately linear, graphical methods of interpolation were employed. In Tables I, II and III are recorded the observed P V values for hydrogen, nitrogen and a 3 : 1 mixture of these gases. In the case of the 3 : 1 mixture the reported PV values were calculated from the observed values obtained with a 74.6–25.4% mixture. Interpolations over the short percentage range seemed

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[10] Lucke and Flather, "Textbook of Engineering Thermodynamics," McGraw-Hill Rook Co., Inc., New York, 1915, p. 299.

[11] Keyes, Joubert and Smith, J. Math. *Phys., Mass. Inst. Tech.*, 1, 191 (1922).

TABLE I

THE COMPRESSIBILITY FACTORS, PV FOR HYDROGEN (PV = 1 AT 1 ATM. AND 0°)

Pressure	Observer	20°	−25°	−50°	−70°
0		1.0719	0.9073	0.8159	0.7428
1		1.0732	,9085	.8170	.7438
25	Bartlett	....	.9230	.8307	.7566
	Schalkwijk	1.0887	...		
	Verschoyle	1.0889	...	...	...
	Holborn	1.0889	.9224	.8303	.7560
	Witkowski	1.0885[a]	.9240	.8330	.7580
50	Bartlett	....	.9384	.8447	.7703
	Schalkwijk	1.1049	...		
	Verschoyle	1.1053	...		
	Holborn	1.1048	.9374	.8447	.7695
	Witkowski	1.1049"	.9382	.8450	.7710
75	Bartlett	1.1215[a]	.9540	.8598	.7852
	Schalwijk	1.1214	...	...	...
	Verschoyle	1.1218	...		
	Onnes	1.1223	...	...	....
	Holborn	1.1217	.9546	.8597	.7842
100	Bartlett	1.1391	.9706	.8756	.8003
	Schalkwijk	1.1382	...		
	Verschoyle	1.1383	...		
	Onnes	1.1402	...	...	...
	Holborn	1.1384	.9695	.8754	.7980
	Amagat	1.1464 1.1385"	...	...	...
125	Bartlett	1.1558	.9867	.8922	.8155
	Verschoyle	1.1550 1.1560"	...	...	...
150	Bartlett	1.1731	1.0034	.9082	.8306
	Verschoyle	1.1717	...		
	Amagat	1.1804 1.1735[a]	...	...	...
200	Bartlett	1.2079	1.0383	.9411	.8640
	Verschoyle	1.2054	...	...	...
	Amagat	1.2154 1.2094[a]	...	...	...
300	Bartlett	1.2799	1.1093	1.0112	.9340
	Amagat	1.2858 1.2817[a]	...	...	...
400	Bartlett	1.3511	1.1808	1.0832	1.0075
	Amagat	1.3578 1.3545"	...	...	...
500	Bartlett	1.4240	1.2542	1.1568	1.0804
	Amagat	1.4320 1.4274"	...	...	...
600	Bartlett	1.4958	1.3272	1.2301	1.1555
	Amagat	1.5057 1.5006"	...	...	...
800	Bartlett	1.6391	1.4717	1.3755	1.3018
	Amagat	1.6504 1.6450[a]	...	...	...
1000	Bartlett	1.7795	1.6139	1.5185	1.4443
	Amagat	1.7923 1.7885[a]	...	...	...

[a] Values by Kohnstamm and Walstra.

TABLE II

THE COMPRESSIBILITY FACTORS, PV, FOR NITROGEN

$PV = 1$ at 1 atmosphere and 0°

Pressure	Observer	20°	−25°	−50°	−70°
0		1.0738	0.9090	0.8174	0.7441
1		1.0735	.9082	.8162	.7432
25	Bartlett	....		...	
	Verschoyle	1.0685	...	...	
	Onnes	1.0689	..	...	...
	Holborn	1.0695	.8910	.7900	.7044
50	Bartlett	....	..	...	.6747
	Verschoyle	1.0667	...	...	
	Onnes	1.0668	.8780	.7680	...
	Holborn	1.0672	.8780	.7672	.6680
	Smith and Taylor	1.0646	...	...	
75	Bartlett	....	.8700	...	.6503
	Verschoyle	1.0685	...	...	
	Onnes	....	...	...	
	Holborn	1.0694	.8714	.7502	.6448
	Smith and Taylor	1.0644	...	...	...
100	Bartlett	1.0745	.8676	.7438	.6362
	Verschoyle	1.0737	...	...	...
	Holborn	1.0766	.8677	.7407	.6290
	Amagat	1.0796	...	...	...
	Smith and Taylor	1.0693	...	...	...
125	Bartlett	1.0836	.8738	.7433	.6340
	Verschoyle	1.0825	...	...	
	Smith and Taylor	1.0784	..	...	
150	Bartlett	1.0963	.8817	.7514	.6430
	Verschoyle	1.0947	...	...	
	Smith and Taylor	1.0906	...	...	
200	Bartlett	1.1320	.9151	.7854	.6823
	Verschoyle	1.1297	...	...	
	Amagat	1.1332	..	...	...
300	Bartlett	1.2293	1.0179	.8986	.8053
	Amagat	1.2290	...	...	...
400	Bartlett	1.3467	1.1445	1.0334	.9477
	Amagat	1.3468	...	...	...
500	Bartlett	...	1.2798	1.1748	1.0914
	Amagat	1.4761	...	...	...
600	Bartlett	1.6098	1.4186	1.3159	1.2331
	Amagat	1.6115	...	...	...
800	Bartlett	1.8817	1.6958	1.5928	1.5111
	Amagat	1.8822	...	...	...
1000	Bartlett	2.1481	1.9600	1.8573	1.7783
	Amagat	2.1527	...	...	...

TABLE III

THE COMPRESSIBILITY FACTORS, P V, FOR A 3:1 MIXTURE OF HYDROGEN AND NITROGEN

$PV = 1$ at 1 atm. pressure and 0°

Pressure	Observer	20°[a]	−25°	−50°	−70°
0		1,0724	0.9077	0.8163	0.7431
1		1.0733	.9084	.8168	.7435
25	Bartlett	....	.9187	.8254	.7510
50	Bartlett	1.1029	.9320	.8367	.7597
	Verschoyle	1.1024	...	...	...
75	Bartlett	....	.9449	.8484	.7704
100	Bartlett	1.1351	.9597	.8618	.7820
	Verschoyle	1.1335	....	....	....
125	Bartlett	....	.9760	.8753	.7951
150	Bartlett	....	,9909	.8903	.8096
200	Bartlett	1.2014	1.0265	.9259	.8433
	Verschoyle	1.2037	...	...	...
300	Bartlett	1.2808	1.1025	1.0007	.9185
400	Bartlett	1.3622	1.1831	1.0837	1.0023
500	Bartlett	....	1.2679	1.1696	1.0901
600	Bartlett	1.5327	1.3547	1.2570	1.1776
800	Bartlett	1.7042	1.5277	1.4309	1.3536
1000	Bartlett	1.8729	1.6986	1,6028	1.5269

[a] Our data in this column are calculated from observed results at 0 and 25°.

justified because of the fact that the P V factor of a mixture of hydrogen and nitrogen is approximately a linear function of the gas composition. The P V values at 1 atmosphere pressure are calculated from the volume–temperature coefficients of the several gases at this pressure.[12]

Discussion of Results

The values shown in the tables represent the mean result of from two to ten independent experiments. Temperature and pressure are easily controlled to within 0.1%. The exact volume of the high pressure pipet is the most difficult factor to determine accurately. However, the data were taken immediately after a careful calibration of the pipet with nitrogen and directly before a second closely agreeing calibration with hydrogen. Experimental evidence from investigations of the compressibility of hydrogen containing 0.9% nitrogen and 5.6% nitrogen proved that the presence of 0.09% of nitrogen can affect the compressibility of pure hydrogen by not more than 1 part in 5000. While no experimental data are available that show the effect of small traces of argon on the compressibility of nitrogen, it is believed that this effect is also so small as to be less than the possible experimental error. The maximum error in the recorded data should not exceed 0.2%.

In the pressure and temperature ranges in which the new data may be

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[12] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, **3,** **6** (1928).

compared with earlier data by other investigators, the agreement is satisfactory. An exception is in non-agreement of the new data for nitrogen at $-70°$ with results interpolated from Holhorn's data at -50 and -100". Here the deviation reaches a maximum of 1.14%.

Temperature and Deviation from the Law of the Ideal Gas

A convenient method of picturing the extent to which a gas under high pressure deviates from the law of the ideal gas is to plot the ratio

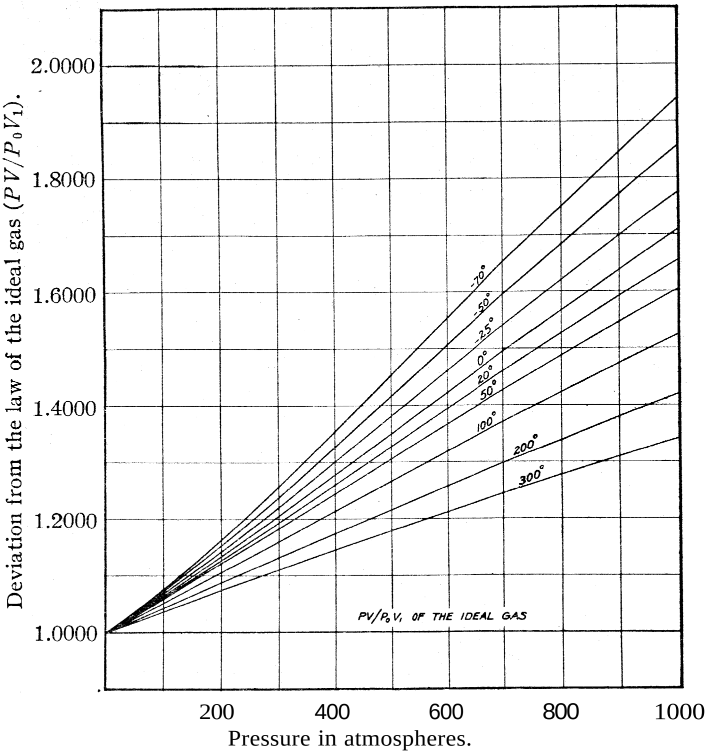

Fig. 2.—Pressure and pressure–volume product for hydrogen.

$(PV/P_0V_1)_T$ against pressure. The PV factor at any temperature T may be taken directly from the tables; the P_0V_1 factor is the P V factor at zero pressure and at the same temperature, T. It is therefore to be found as the first item in each column of the table. This results in bringing all the PV–P isotherms to a common origin. For the ideal gas the ratio $(PV/P_0V_1)_T$ is equal to unity. Figures 2, 3 and 4 show the deviations for hydrogen, nitrogen and the 3 : 1 mixture, respectively, In these diagrams are also included the results of previous work in this Laboratory[1] on these gases at 0° and higher temperatures. Especially interesting is the point at about 380 atmospheres' pressure where nitrogen exhibits approximately the same deviation at all temperatures from —70 to 100°. Obviously such a phenomenon cannot continue through an indefinite range of temperature, for the deviation pressure curve must approach with increasing temperature the horizontal line where the ratio $(PV/P_0V_1)_T$ is

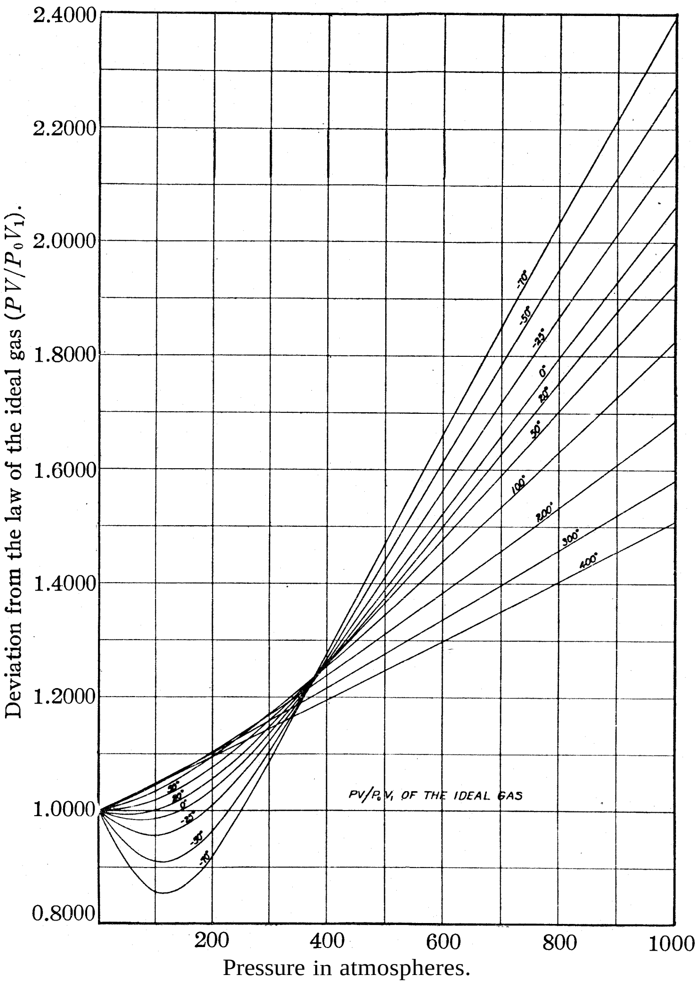

Fig. 3.—Pressure and pressure–volume product for nitrogen.

unity. At 200° and higher temperatures the deviation curves "fan out" toward the ideal gas isotherm. It is apparent, in the light of experimental data, that the general statement "a gas more nearly conforms to the law of the ideal gas with increasing temperature," must be modified somewhat, for in the case of nitrogen and of any other gas that exhibits a similar dip in the deviation–pressure curve, there are pressures and temperatures at which the deviation increases with temperature to a well-defined maximum. The methods by which the PV data in Tables I, II and III may be used in the solving of practical pressure–volume–temperature problems of laboratory or plant were presented in an earlier report.'

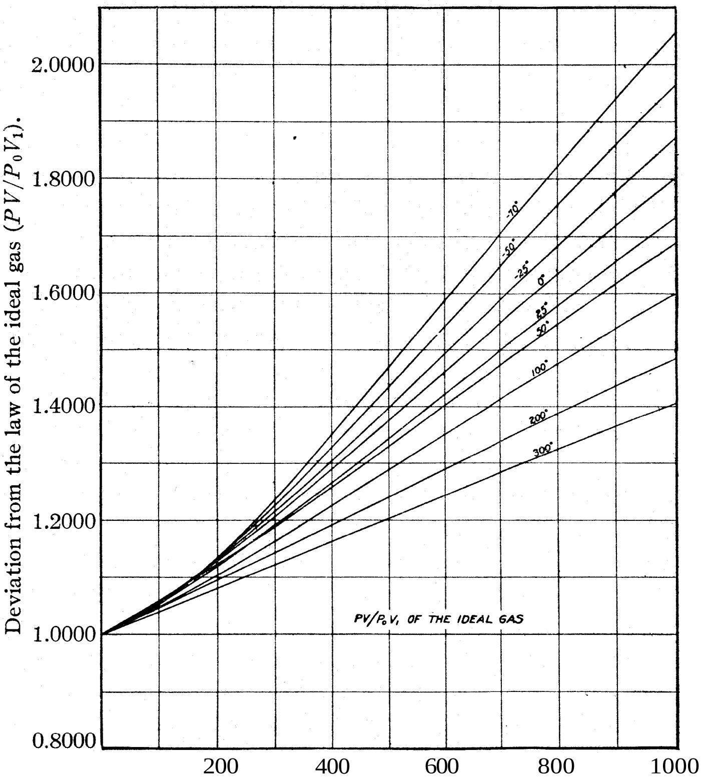

Fig. 4.—Pressure and pressure–volume product of a 3:1 hydrogen–nitrogen mixture.

The authors wish to express appreciation to the staff of the Fixed Nitrogen Research Laboratory for their interest and for their efficient help in paving the way to the successful conclusion of this investigation.

Summary

The compressibility isotherms of hydrogen, nitrogen and a 3:1 mixture of these gases each at 20, −25, −50 and −70° have been presented. In the case of nitrogen, a curious phenomenon appears at about 380 atmospheres' pressure where the deviation from the law of the ideal gas is nearly constant through the temperature range −70 to +100°.

WASHINGTON, D. C.

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

THE COMPRESSIBILITY ISOTHERMS OF CARBON MONOXIDE AT TEMPERATURES FROM -70 TO 200° AND AT PRESSURES TO 1000 ATMOSPHERES

BY EDWARD P. BARTLETT, HARRY C. HETHERINGTON, HAMLINE M. KVALNES AND THOMAS H. TREMEARNE

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The advent of commercial processes involving the use of gases under extreme conditions of temperature and pressure has placed carbon monoxide side by side with nitrogen and hydrogen in interest and importance. Carbon monoxide constitutes one-half the volume of pure water gas which is now the principal source of hydrogen used in ammonia synthesis. It is also a primary factor in the catalytic synthesis of methanol and other organic compounds that are rapidly assuming tremendous commercial importance.

Very little reliable information is available regarding the physical properties of compressed carbon monoxide. Natterer[1] in 1855 reported an investigation of the compressibility of this gas at pressures between 77 and 2790 atmospheres. His results are relative to a PV value of 1.000 at 77 atmospheres; the temperature is not stated. Amagat[2] investigated the compressibility of carbon monoxide at pressures from 24.1 to 304.1 atmospheres at temperatures ranging from 18 to 22°. His results are presented in arbitrary units and show only changes in the PV factor with change in pressure. Very recently, Scott[3] has presented data for the 25° isotherm of carbon monoxide at pressures to 170 atmospheres. Botella[4] has determined the isotherms at 0, 12.44 and 20.22' at pressures to 130 atmospheres, and Goig[4a] has collected data at 0° at pressures between 50 and 130 atmospheres. It is apparent that four investigations of the $P-V-T$ relationships of carbon monoxide were proceeding simultaneously and independently. Scott employs a method similar to that used at the Fixed Nitrogen Research Laboratory and at the Physikalische Technische Reichsanstalt of Berlin. Botella and Goig follow in general the method used by Amagat and by the staff of the Cryogenic Laboratory at Leiden. The results obtained in the three investigations are incorporated in our table of results in cases where they cover corresponding ranges of pressure and temperature. In general, our results are from 0.2 to 0.3% higher than those of Scott, Botella or Goig.

It was the purpose of the present investigation to obtain accurate data

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[1] Natterer, *Pogg. Ann.*, 94, 436 (1855).

[2] Amagat, *Ann. chim. phys.*, [5] 19, 345 (1880).

[3] Scott, *Proc. Roy. Soc.* (London), 125A, 330 (1929).

[4] Botella, *Anales soc. españ. fís. quím.*, 27, 315 (1929).

[4a] Goig, *Compt. rend.*, 189, 246 (1929)

on the compressibility of this gas over a wide enough range of pressure and temperature to meet the present industrial demands. The results also furnish further material for the testing of equations of state for real gases, which are important in theoretical chemistry and in thermodynamic calculations. They also make possible further comparison of the physical properties of carbon monoxide and nitrogen, substances designated as "isosteres," because of their similar electronic structure.[5] The similarity of physical properties of the two gases is very evident at moderate and low pressures even to their temperatures of liquefaction. The new data show the analogy to hold qualitatively at pressures to 1000 atmospheres.

Method.—A quantity of gas at known pressure and temperature is confined in a pipet of known capacity. The gas is allowed to expand into a gas buret maintained at constant temperature and the quantity of gas is determined by measurement of a fixed volume at a measured pressure, not far above or below atmospheric pressure.

Preparation and Purification of the Gas.—Carbon monoxide was prepared in this Laboratory by J. G. Thompson and P. G. Kosting.[6] The method involves the decomposition of formic acid according to the process

$$HCOOH \longrightarrow CO + H_2O \qquad (1)$$

by means of phosphoric acid at 170°. The carbon monoxide was purified from traces of undecomposed acid by sodium hydroxide, then collected in a large steel holder from which it was compressed into steel cylinders to 100 atmospheres. The water in the holder was covered with a layer of heavy mineral oil to retard the diffusion of dissolved air from the water into the gas. Analyses of the carbon monoxide in the steel cylinders by the Orsat method indicated the gas to be free from impurities to within the limits of experimental accuracy. However, later analyses by Kvalnes' low pressure method[7] indicated a possible 0.08–0.10% impurity in the gas from the 100-atmosphere cylinders, while no impurity could be detected in the gas from the gas generator. It is possible that traces of air were introduced during compression.

While it appears possible to produce pure carbon monoxide, impurities are found when it is stored over a period of time in contact with iron. It is believed that the use of copper gas holders, bronze compressors and cylinders and copper lined conduits would have obviated most of the difficulty, but unfortunately such equipment was not available without unjustifiable expense. It was found more expedient to handle the gas quickly and remove the impurities in a purification train under high pressure just before the final measurements were made.

Carbon monoxide is in a metastable condition at moderate and low tem-

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[5] Langmuir, THIS JOURNAL, 41, 1543 (1919).

[6] Thompson, *Ind. Eng. Chem.*, 21, 389 (1939).

[7] This method will be described in a separate report.

peratures. It needs but a proper catalyst to bring about the partial decomposition represented by the expression

$$2\text{CO} \longleftrightarrow \text{C} + \text{CO}_2 + 41{,}950 \text{ cal.}\text{[8]} \qquad (2)$$

According to Lewis and Randall the change in free energy (ΔF°) of this reaction at 25° is —29,240 cal. The equilibrium constant (K) may then be calculated from the equation

$$(\Delta F^\circ)_{298} = -RT \ln K \qquad (3)$$

where K is the constant in the expression

$$[\text{CO}_2]/[\text{CO}]^2 = \text{K} \qquad (4)$$

The value of K is found to be 2.65×10^{21}, from which it is calculated that at atmospheric pressure and 25° only $2 \times 10^{-8}\%$ of carbon monoxide is in equilibrium with carbon and carbon dioxide.

High pressure and low temperature favor the formation of carbon dioxide, but low temperature retards the speed with which the reaction takes place. Iron, even in the massive form in which it is present in the gas holder, appears to act as a catalyst for the reaction.[9] Pure carbon monoxide, allowed to stand in the holder exposed to direct sunlight in warm weather for three days, decomposed to such an extent that it could not be used for compressibility measurements without overtaxing the capacity of the purification train. Cylinders of the gas at 100 atmospheres' pressure acquire a carbon dioxide content of over 1% after standing in a protected location for two or three weeks. In addition to this phenomenon carbon monoxide forms with iron, iron carbonyl (Fe(CO)_5), a compound that has received much attention recently, first as a source of pure iron[10] and as an anti-detonant[8] in internal combustion engines and, second, as an undesirable impurity in the carbon monoxide gas used in catalytic processes. When this impurity is present large quantities of carbon dioxide appear. The exact mechanism of the reaction is apparently not yet understood. The iron carbonyl itself may be the decomposition catalyst, or the iron carbonyl first formed may decompose, giving catalytically active finely divided iron. The authors are inclined to accept the first explanation. They believe that it more logically accounts for the rapid decomposition of carbon monoxide in the holder and cylinders at room temperature. In order to test this conclusion qualitatively two glass balloon flasks of liter capacity were filled with carbon monoxide. Into one of the flasks was introduced a few drops of a commercial preparation containing iron carbonyl dissolved in a hydrocarbon. After about fifteen days the gases were tested for carbon dioxide. Quantities of carbon dioxide were present in

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[8] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 574.

[9] J. H. Frydlender, *Rev.* prod. *chim.*, 29, 1 (1926).

[10] I. G. Farbenind A. G., Brit. Patents 269,345, May 10, 1926; 268,770, April 1, 1926; 269,677, Jan. 23, 1926; 281,963, June 25, 1927.

the flask containing the iron carbonyl, The carbon monoxide in the other flask showed no trace of decomposition. No traces of metallic iron appeared in the flask containing the iron carbonyl. Its presence, however, possibly could have been masked by the very evident reddish-brown precipitate that answers to the description of $Fe(CO)_9$.[11] Evidence against our conclusion lies in the fact that carbon dioxide forms rapidly in a steel cylinder at 300°, a temperature which is well above the temperature at which iron carbonyl is stable. It is possible that both iron and iron carbonyl catalyze carbon monoxide decomposition.

Iron carbonyl is an amber colored liquid, with boiling point at 102.5' and freezing point at $-21°$. According to the literature[12] it is decomposed into iron and carbon monoxide at 216°. The authors undertook to remove traces[13] of iron carbonyl from carbon monoxide by means of hot porcelain at about 450°. The result was definite and perhaps to be expected. Carbon dioxide appeared in such quantities as to make its removal practically impossible and the furnace tube shortly became clogged with a mixture of carbon and iron, analyzing in the ratio of about 64 to 1 by weight. More successful were attempts to freeze out the iron carbonyl. For this purpose a deep trap was constructed which was kept continually at a temperature of about $-80°$ by means of a mixture of acetone and carbon dioxide snow. The small diameter intake tube of this trap frequently clogged with solid iron carbonyl. The plug of solid material was removed by applying heat to the tube in conjunction with a large differential pressure.

The carbon monoxide was compressed to high pressure with the same apparatus employed for nitrogen and hydrogen,[14] a description of which appears in earlier reports from this Laboratory. The apparatus from the storage tower of the compression system to and including the high pressure pipet was constructed of bronze.[15] The conduit tubes were copper lined and the hardened valve stems copper plated.

From the high pressure storage cylinder the gas passed through a trap maintained at 0° with ice to remove the bulk of the water vapor, through a tower of crushed fused potassium hydroxide to remove carbon dioxide and

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[11] J. N. Friend, "A Text-Book of Inorganic Chemistry," Vol. IX (11), J. B. Lippincott Co., Philadelphia, **1921,** p. 198.

[12] Bloxam, "Chemistry, Inorganic and Organic," 10th ed., **1913,** p. 456.

[13] Griffith and Holliday [*J. Soc.* Chem. *Ind.*, **47,** 311T (1928)] found 0.07% of iron carbonyl in carbon monoxide which had been compressed from a steel storage holder, and much less than this in carbon monoxide which had been stored for six months in twenty-year old steel cylinders.

[14] (a) Bartlett, THIS JOURNAL, 49, 68 (1927); (b) *ibid.*, **49,** 687 (1927); (c) ibid., **49, 1955** (1927); (d) Bartlett, Cupples and Tremearne, *ibid.*, **50,** 1275 (1928).

[15] The physical properties of this material are discussed in a report from this Laboratory dealing with the compressibility isotherms of nitrogen and hydrogen [THIS JOURNAL, **52, 1363** (1930)].

more water vapor,[16] through the cold trap at −80° to remove iron carbonyl and traces of water vapor, and finally through a second tower of potassium hydroxide to remove any remaining traces of carbon dioxide. The gas was tested frequently at this point for carbon dioxide by means of a saturated solution of barium hydroxide. It was also tested for iron carbonyl. The presence of even traces of this impurity impart a yellow color to the otherwise brilliant blue carbon monoxide flame. Whenever the tests showed the presence of carbon dioxide the caustic towers were refilled. In general no difficulty was experienced in reducing the iron carbonyl content to a point where it gave but the faintest yellow tinge to the tip of the flame.

TABLE I

THE COMPRESSIBILITY FACTORS, PV, FOR CARBON MONOXIDE

$PV = 1$ at 1 atm. pressure and 0°

Results marked S are by Scott; results marked B are by Botella; results marked by G are by Goig

Atm.	−70°	−50°	−25°	0°	25°	50°	100°	150°	200°
0	0.7441	0.8173	0.9089	1.0004	1.0920	1.1837	1.3668	1.5498	1.7329
1	.7427	.8162	.9082	1.0000	1.0918	1.1836	1.3671	1.5504	1.7336
25	.7030	.7903	.8938	0.9894	1.0866	1.1822	1.3752	1.5696	1.7577
	....	....	....	.	S 1.05	....	....	....	....
50	.6636	.7622	.8768	.9796	1.0831	1.1826	1.3837	1.5823	1.7758
	....	....	....	G .9763	S1.0797	....	....	....	....
	....	....	....	B .9766	B1.0807	....	....	....	....
75	.6323	.7388	.8632	.9740	1.0832	1.1882	1.3946	1.5977	1.7948
	....	....	....	G .9708	S1.0797	....	....	....	....
	....	....	....	B .9713	B1.0815	....	....	....	....
100	,6147	,7264	,8592	.9745	1.0864	1.1955	1.4062	1.6151	1.8146
	....	....	....	G .9704	S1.0836	....	....	....	....
	....	....	....	B .9705	B1.0852	....	....	....	....
125	.6108	.7247	.8598	.9797	1.0950	1.2069	1.4220	1.6316	1.8357
	....	....	....	B .9751	S1.0927	....	....	....	....
	....	....	....	G .9751	....	....	....	....	....
150	.6190	.7304	.8663	.9889	1.1085	1.2192	1.4388	1.6537	1.8598
	....	....	....	....	S1.1050	....	....	....	....
200	.6631	.7656	,9022	1.0200	1.1415	1.2561	1.4794	1.6987	1.9090
300	.7955	.8872	1.0087	1.1211	1.2406	1.3521	1.5798	1.8054	2.0183
400	.9434	1.0285	1.1403	1.2487	1.3625	1.4716	1.6963	1.9178	2.1380
500	1.0920	1.1755	1.2831	1.3843	1.4940	1.6023	1.8235	2.0450	2.2627
600	1.2386	1.3225	1.4282	1.5256	1.6317	1.7378	1.9557	2.1757	2.3923
800	1.5236	1.6100	1.7153	1.8064	1.9915	2.0144	2.2244	2.4442	2.6602
1000	1.7992	1.8871	1.9935	2.0827	2.1857	2.2879	2.4935	2.7142	2.9264

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[16] Judging from the deep coloration on the caustic at the intake end of this tower, it appears that there must be also some iron carbonyl decomposition at this point.

Experimental Results

The pressure–volume–temperature relationships are expressed in Amagat units. The unit gas mass is that mass of gas occupying 1 liter at 0° and at a pressure of 1 atmosphere. PV is therefore equal to unity under these conditions. The PV values at 1 atmosphere at other than 0° are calculated from the known temperature–volume coefficient of carbon monoxide.[17] All other values given in Table I are unsmoothed experimental results involving no interpolations or extrapolations with the exception of a few data at 100 and 200°, where due to a thermometer correction interpolations were made over a maximum range of 0.3'. The methods of applying these data to pressure–volume–temperature problems in laboratory or plant are presented in an earlier report.[14d]

Temperature and Deviation from the Laws of the Ideal Gas.—The deviation of a gas from the law of the ideal gas is conveniently expressed in the form of a ratio $(PV)/(P_0V_1)_T$ in which $(PV)_T$ is the pressure–volume product at T degrees, referred to unity at 0° temperature and 1 atmosphere pressure, while $(P_0V_1)_T$ is the pressure–volume product at zero pressure at the temperature T. The values of $(P_0V_1)_T$ may be found as the first item in each column of Table I. The results for carbon monoxide are shown in Fig. 1. In order to avoid confusion on the diagram, the experimental points on the curves are not shown. However, every item in Table I has been used in calculating these points and the curves shown pass through every plotted point. The original diagram was of such size that the error in plotting could not exceed 0.1 to 0.2%, while the maximum error of observation is believed not to exceed 0.2 to 0.3%.

Discussion of Results

It is apparent from a study of the curves for carbon monoxide in Fig. 1 and a similar family of curves for nitrogen[15] that the two gases exhibit very similar compressibility phenomena. Carbon monoxide is slightly more compressible in the low pressure range and slightly less compressible in the high pressure range. This is to be expected from the fact that carbon monoxide has a slightly higher critical temperature (−139.0°) than nitrogen (−147.1'). In general, the difference in compressibility becomes less with increasing temperature. These experimental facts are well illustrated in Fig. 2, in which the deviations from the ideal gas law for the two gases at a number of pressures are plotted against temperature. Results for hydrogen are included on the chart to emphasize further the similarity of carbon monoxide and nitrogen.

In a report now published[15] it is pointed out that in the temperature range −70 to 100° and at a pressure of 380 atmospheres, nitrogen exhibits

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[17] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. III, p. 16.

approximately a constant deviation from the law of the ideal gas. At this pressure, therefore, and in this temperature range, PV, and hence V, is a linear function of the absolute temperature, a major criterion in the definition of an ideal gas. The family of curves in Fig. 1 shows that carbon monoxide exhibits a similar phenomenon at a pressure of 375 atmospheres and through even a wider range of temperature, −70 to 200°. It can be predicted with certainty that at higher temperatures the deviation curves will "fan out" toward the perfect gas isotherm in a manner similar to curves for nitrogen and hydrogen. In order to establish whether the unique point phenomenon exhibited by nitrogen and carbon monoxide is characteristic of other gases, the available PV data for carbon dioxide, ethylene and oxygen[18] have been investigated. The phenomenon in the case of these gases is not sufficiently evident to justify the statement that it exists.

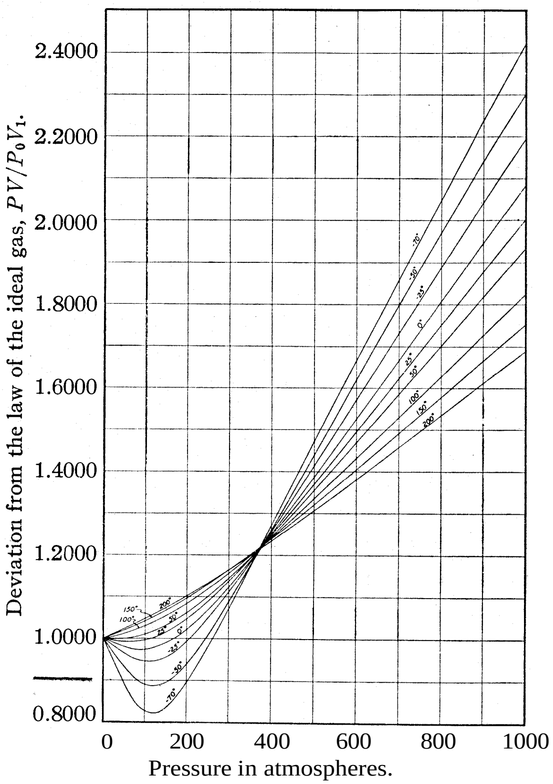

Fig. 1.—Pressure and pressure–volume product of carbon monoxide, $(PV/P_0V_1)_T$.

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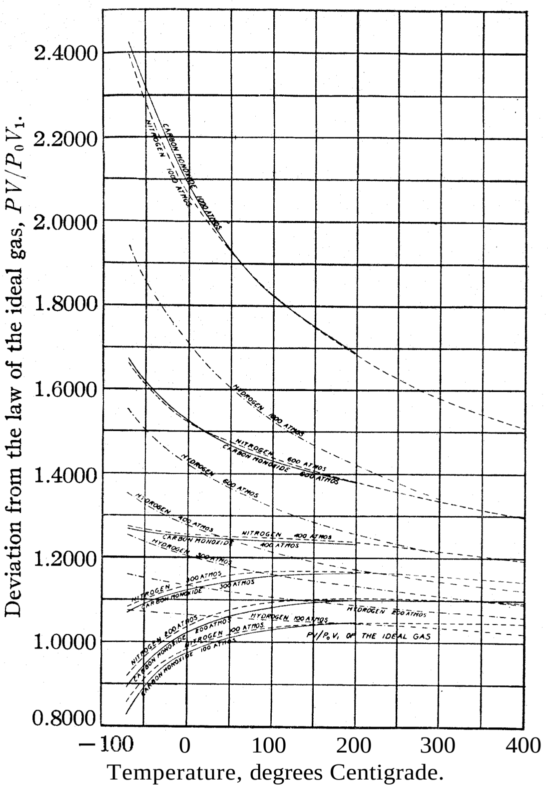
[18] "International Critical Tables," McGraw-Hill Book Co., Inc., New York 1928, Vol. III, p. 3 *et seq.*

The authors are indebted to the staff of the Fixed Nitrogen Research Laboratory for suggestions and for coöperation in the solving of the many problems met with in this investigation.



Hydrogen, — ‑ — ‑; nitrogen, — — — —; carbon monoxide, ———.

Fig. 2.—Temperature and deviations from the law of the ideal gas.

Summary

This report has presented the compressibility factors of carbon monoxide at temperatures from –70 to 200° and at pressures to 1000 atmospheres. The results show carbon monoxide to be similar to nitrogen in physical properties at high pressure. In the low pressure range, carbon monoxide is slightly more compressible than nitrogen, while in the high pressure range it is slightly less compressible. At about 375 atmospheres' pressure the deviation of carbon monoxide from the law of the ideal gas is approximately constant (1.217) through the 270° range of temperature. At this pressure

the volume of a given gas mass of carbon monoxide is a linear function of the absolute temperature.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

THE CONSTANTS OF THE BEATTIE–BRIDGEMAN EQUATION OF STATE WITH BARTLETT'S P-V-T DATA ON NITROGEN

BY W. EDWARDS DEMING AND LOLA E. SHUPE

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In connection with recent work in high pressure on gases it has been deemed advisable to test some of the recently proposed equations of state. Bartlett has extended his P–V-T measurements on nitrogen and several other gases to include -25, -50, and $-70°$ up to 1000 atmospheres pressure. At pressures below 100 atmospheres data were obtained by Bartlett at this laboratory only sufficient to check the work of other investigators in this low pressure range. The low pressures in Table III were compiled from data furnished by the Reichsanstalt, the Leiden laboratory, and the Massachusetts Institute of Technology. With this complete set of data an equation of state can now be tested throughout a wider range of pressure, volume, and temperature than has hitherto been possible. The Beattie–Bridgeman[1] equation of state was chosen because its propounders have indicated that it reproduces the trends and measurements very well, and because its utility is great, once the constants have been determined, due to its relatively simple algebraic form.

In this discussion P denotes pressures in atmospheres, v denotes specific volumes in cc. per g., and r, the gas constant in cc. atm. per g. per degree. The gas that Bartlett used for these measurements contained 0.07% argon and 99.93% nitrogen. The presence of the argon makes the value of r slightly different from that for pure nitrogen, but ought to have no discernible effect on any of the other constants in the equation of state. The value of r for this gas is 2.92861 cc. atm. per g. per degree.

Since Bartlett's data[2] are listed in the form of isotherms, they were first converted into isochores, by Andrews' method,[3] because this form is better adapted to the determination of the constants in an equation

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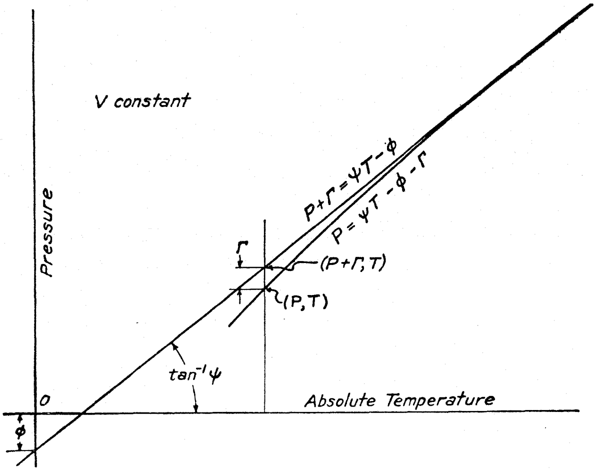
[1] Beattie and Bridgeman, Proc. *Am. Acad. Arts Sci.*, **63**, 229 (1928); THIS JOURNAL, **49**, 1665 (1927); and later papers.

[2] Bartlett, Cupples, and Tremearne, *ibid.*, 50, 1275 (1928). Bartlett and his collaborators have since interpolated these data to even temperatures, and their observations have been extended to include -70, -50, -25, and 20°. These are published in the preceding article.

[3] Andrews, *Phil. Trans. Roy. Soc.*, *166*, 421 (1876). This method is clearly explained by O. C. Rridgeman, THIS JOURNAL, **49**, 1130 (1927).

of state that is solved explicitly for P. The observed pressures at even volumes are listed in Table III, the digit in the last decimal place being doubtful. Interpolated pressures can be made more reliable than the original observations by carefully smoothing the curves used in the process of interpolation. Isochores at $v = 3, 4, 5, 7.5, 10, 12.5, 15, 20, 25, 30$ and 40 were chosen as being sufficiently representative of Bartlett's data, for our purpose.



Pig. 1.—General shape of a nitrogen isochore.

The smaller the range of pressure, volume, and temperature that is used to determine the constants in any equation, the better will be the fit *over that range.* We have sought those values of the constants that will reproduce pressures with an accuracy of a few tenths of a per cent. from the lowest pressures to the highest pressures at which the formula will yield results of the desired accuracy. Accordingly we have favored the high-pressure, low-temperature data as far as is possible without destroying the fit at low pressures.

Following Beattie and Bridgeman's scheme, we write

$$P + \Gamma = \psi T - \phi \tag{1}$$

ψ and ϕ are functions of v; Γ is a function of v and of T. The isochores for high volumes are almost straight lines, but with lower volumes curvature sets in at the low temperature end, as shown in Fig. 1. Γ may be looked upon as a correction term, one that when added to P straightens the isochore. (1) Is the equation of this straight line in the variables $P + \Gamma$ and T, ψ being the slope and ϕ the negative intercept on the P axis. Beattie and Bridgeman put

$$\left.\begin{array}{lll} \Gamma T^2 = \psi c/v & \psi = R(v + B)v^{-2} & \phi = Av^{-2} \\ B = B_0(1 - b/v) & A = A_0(1 - a/v) & \end{array}\right\} \tag{2}$$

with A_0, B_0, a, b, c constants, mentioning the possibility of extending the expressions for A and B to include higher powers of $1/v$.

The problem is to find the best values of ψ, ϕ, c and hence of B, A, c, for each isochore, and then to express B and A by series in $1/v$ with as few terms as practicable; c is supposed to be constant and hence independent of v. By best values, we shall mean those that render $(1/n)\Sigma(P_{\text{obs.}} - P_{\text{calcd.}})^2/P^2_{\text{obs.}}$ or $(1/n)\Sigma(\%\ \text{dev.})^2$ a minimum along any isochore. For any isochore, $\Sigma(\%\ \text{dev.})^2$ is a function of ψ, ϕ, c. (Dev. = deviation = $P_{\text{obs.}} - P_{\text{calcd.}}$. n is the number of temperatures at which pressure is measured along any isochore, ten in Bartlett's data.) The process of finding the best values of ψ, ϕ, c for any isochore is formally the same as Least Squares with the observations on v and T considered infallible compared with those on P. Dr. Bartlett considers his measurements on v to be less reliable than those on P and T. Accordingly, if only one of the three variables P, v, T is to be adjusted, it should be v. However, this is impracticable because the equation of state cannot be solved explicitly for v. Our method, therefore, must not be called Least Squares.

In the language of mathematics, it would be customary to call the values of ψ, ϕ, c that minimize $(1/n)\Sigma(\%\ \text{dev.})^2$ the critical values, and the minimum an absolute minimum. Critical and best are here synonymous. With a particular value of ψ, ϕ, or c, not its critical value, the minimum will be constrained or relative, and will be larger in value than the absolute minimum. Closeness of fit at isolated points is not the only thing required in fitting an equation; the trends or derivatives must also be reproduced. When $\Sigma(\%\ \text{dev.})^2$ is small, the trend as well as the actual pressures is accurately represented. This is in contrast with $\Sigma(\%\ \text{dev.})$, which might be zero for an isochore while the trends are inaccurately represented. Thus with deviations −4, +4, −3, +3, 0, 5, −5, $\Sigma(\%\ \text{dev.}) = 0$, $\Sigma\ (\%\ \text{dev.})^2 = 100$, and derivatives obtained from such a fit would be entirely misleading.

The critical values of ψ, ϕ, c for v = 5, 7.5, 10, 12.5 are listed in Table I.

TABLE I

CRITICAL VALUES OF ψ, ϕ, c AND THE ABSOLUTE MINIMUM OF $(1/10)\Sigma(\%\ \text{DEV.})^2$ FOR FOUR LOW VOLUMES

v	ψ	ϕ	c	$(1/10)\Sigma(\%\ \text{dev.})^2$
5	0.8162825	57.167	1.848×10^6	0.1191
7.5	.4869524	26.042	2.077	.0431
10	.3451921	14.6366	2.313	.0185
12.5	.2670248	9.3459	2.477	.0086

c has an upward trend with increasing v, so it is necessary to give it an average value. Pressures calculated at the higher volumes are not very sensitive to changes in c, so an average of the critical values of c for the four low volumes of Table I was taken. $c = 2.2 \times 10^6$ was used in the subsequent work.

The next task is to determine what values of ψ and ϕ with $c = 2.2 \times 10^6$ render $(1/10)\Sigma(\%\ \text{dev.})^2$ a (relative) minimum for each isochore. The values found are used to compute $B = (\psi v^2 - rv)/r$ and $A = \phi v^2$ for each volume. These, together with the absolute and relative minimum values of $(1/10)\Sigma(\%\ \text{dev.})^2$, are shown in Table II.

TABLE II

VALUES OF ψ AND ϕ THAT RENDER $(1/10)\Sigma(\%\ \text{DEV.})^2$ A (RELATIVE) MINIMUM WITH $c = 2.2 \times 10^6$, FOR EACH ISOCHORE, AND THE VALUES OF B AND A COMPUTED THEREFROM. RELATIVE AND ABSOLUTE MINIMUM VALUES OF $(1/10)\Sigma(\%\ \text{DEV.})^2$

			Minimum of $(1/10)\Sigma(\%\ \text{dev.})^2$			
v	ψ	ϕ	Relative	Absolute	B	A
3	1.683837	137.911	0.38710	....	2.1747	1241.2
4	1.100409	82.863	.23570	....	2.0119	1325.8
5	0.8126459	55.263	.12896	0.11911	1.9371	1381.6
7.5	.4866500	25.8571	.04448	.04313	1.8471	1454.5
10	.3454291	14.7938	.01984	.01851	1.7950	1479.4
12.5	.2673827	9.5385	,00936	.00862	1.7657	1490.4
15	.2179586	6.6577	.00582	....	1.7454	1498.0
20	.1590196	3.7642	.00314	....	1.7195	1505.7
25	,1251262	2.4145	,00209	....	1.7034	1509.1
30	.1031291	1.6794	.00155	....	1.6929	1511.5
40	.0762905	0.9464	.00106	....	1.6801	1514.2

The values of A and B from this table are plotted as functions of $1/v$ in Fig. 2. If every A and B point within a given range lay on a straight line, it would be a simple matter to finish fitting the equation over *that range.* The problem of placing the straight lines in Fig. 2 is not one in

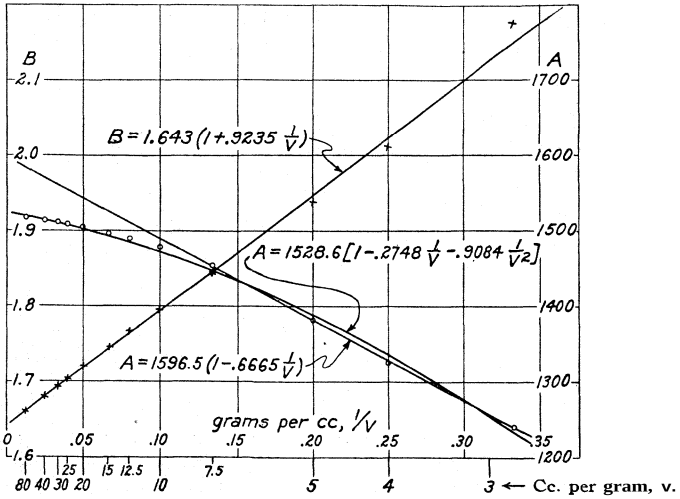


Fig. 2.—The B and **A plots.**

TABLE III

OBSERVED PRESSURES AS INTERPOLATED FROM BARTLETT'S DATA BY ANDREWS' METHOD, AND THE COMPARISON WITH PRESSURES CALCULATED FROM THE BEATTIE–BRIDGEMAN EQUATION OF STATE

Deviations (i) are computed with ϕ determined by the straight line; (ii), by the parabola. Pressures are in atmospheres; volumes are in cc. per g. R. M. S. denotes root mean square. All calculations are rounded off finally to the number of figures shown.

Vol.	T°K. T°C.	203.13 −70	223.13 −50	248.13 −25	273.13 0	293.13 20	323.13 50	373.13 100	473.13 200	573.13 300	673.13 400	R. M. S. deviation, %
3	P obs.	175.89	212.01	258.78	303.07	339.30	394.51	485.07	659.06	824.84	987.86	
	(i) % dev.	1.89	0.39	0.38	−0.03	0.14	0.73	1.39	1.49	0.77	0.08	0.957
	(ii) % dev.	1.41	.00	.06	− .30	− .11	.52	1.22	1.37	.67	− .01	.785
4	P obs.	126.88	150.15	179.76	208.17	231.57	267.28	324.92	438.20	547.08	653.37	
	(i) % dev.	0.65	−0.31	−0.42	−0.78	−0.58	0.02	0.35	0.58	0.06	−0.63	.498
	(ii) % dev.	.95	− .05	− .20	− .59	− .41	.17	.47	.67	.13	− .57	.500
5	P obs.	101.63	118.64	140.22	161.11	178.22	204.37	246.43	329.09	409.88	488.93	
	(i) % dev.	0.36	−0.33	−0.38	−0.62	−0.45	0.10	0.29	0.31	−0.01	−0.55	.381
	(ii) % dev.	.56	− .15	− .23	− .49	− .33	.20	.38	.38	.04	− .51	.364
7.5	P obs.	69.77	79.72	92.47	104.97	115.02	130.26	155.10	204.23	252.70	300.48	
	(i) % dev.	0.37	−0.15	−0.09	−0.14	−0.07	0.20	0.28	0.26	0.05	−0.29	.215
	(ii) % dev.	.20	− .30	− .21	− .25	− .18	.11	.21	.20	.00	− .32	.216
10	P obs.	53.64	60.67	69.67	78.51	85.57	96.24	113.76	148.57	182.99	217.11	
	(i) % dev.	0.41	0.03	0.13	0.11	0.12	0.26	0.28	0.26	0.08	−0.15	.214
	(ii) % dev.	.09	− .25	− .12	− .11	− .09	.08	.13	.14	− .01	− .23	.143
12.5	P obs.	43.666	49.107	56.022	62.850	68.284	76.487	89.982	116.897	143.557	170.039	
	(i) % dev.	0.39	0.14	0.21	0.21	0.20	0.29	0.26	0.24	0.10	−0.09	.229
	(ii) % dev.	.02	− .19	− .07	− .05	− .04	.07	.08	.10	− .01	− .18	.102
15	P obs.	36.854	41.284	46.898	52.450	56.861	63.521	74.487	96.411	118.157	139.780	
	(i) % dev.	0.37	0.19	0.25	0.25	0.22	0.29	0.24	0.23	0.11	−0.05	.235
	(ii) % dev.	.00	− .15	− .04	− .01	− .02	.07	.05	.08	− .01	− .15	.079
20	P obs.	28.111	31.340	35.411	39.447	42.651	47.487	55.465	71.439	87.312	103.123	
	(i) % dev.	0.33	0.22	0.27	0.27	0.23	0.27	0.21	0.20	0.10	−0.02	.230
	(ii) % dev.	− .02	− .09	.00	.03	.01	.07	.03	.06	− .01	− .11	.056

TABLE III (*Concluded*)

Vol.	T°K.	203.13	223.13	248.13	273.13	293.13	323.13	373.13	473.13	573.13	673.13	R. M. S. deviation, %
	T°C.	−70	−50	−25	0	20	50	100	200	300	400	
25	P obs.	22.730	25.267	28.457	31.626	34.140	37.935	44.203	56.763	69.258	81.714	
	(i) % dev.	0.29	0.22	0.26	0.26	0.22	0.25	0.18	0.17	0.09	0.00	.212
	(ii) % dev.	− .02	− .06	.01	.04	.02	.06	.02	.05	− .01	− .09	.046
30	P obs.	19.080	21.169	23.790	26.397	28.467	31.589	36.751	47.097	57.398	67.672	
	(i) % dev.	0.26	0.21	0.24	0.25	0.21	0.23	0.16	0.15	0.08	0.00	.194
	(ii) % dev.	− .02	−0.05	.02	.04	.02	.06	.01	.04	− .01	− .07	.040
40	P obs.	14.444	15.986	17.918	19.842	21.371	23.675	27.491	35.139	42.761	50.368	
	(i) % dev.	0.20	0.18	0.21	0.21	0.18	0.19	0.13	0.12	0.07	0.01	.162
	(ii) % dev.	− .02	− .03	.02	.05	.02	.05	.01	.03	− .01	− .06	.033
(i) R. M. S. dev. %		0.674	0.234	0.277	0.353	0.274	0.307	0.480	0.523	0.243	0.274	
(ii) R. M. S. dev. %		.546	.151	.122	.263	.173	.186	.417	.480	.205	.275	
V		1.6432	1.7535	1.8903	2.0273	2.1451	2.3283	2.6194	3.1929	3.7367	4.2611	
P obs.		600	600	600	600	600	600	600	600	600	600	
(i) % dev.		28.7	19.7	12.4	7.76	5.77	4.30	2.47	1.12	0.10	−0.73	
(ii) % dev.		16.9	11.5	7.04	4.19	3.26	2.84	1.88	1.08	.16	− .66	
V		1.4218	1.4850	1.5671	1.6503	1.7175	1.8249	1.9947	2.3356	2.6547	2.9762	
P obs.		1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	
(i) % dev.		42.8	33.3	25.1	19.3	15.9	12.6	8.48	4.40	1.51	0.12	
(ii) % dev.		27.9	21.4	16.0	12.4	10.3	8.67	6.12	3.54	1.19	.02	

curve-fitting; they should be drawn with a view to giving a good fit over a limited range rather than a barely passable fit over a long range. The lines drawn in Fig. 2 give

$$\left.\begin{array}{ll} A_0 = 1596.5 & a = 0.6665 \\ B_0 = 1.643 & b = -0.9235 \\ \text{which with } c = 2.2 \times 10^6 & \end{array}\right\} \qquad (3)$$

are the values that we have determined for the five constants. The values that Beattie and Bridgeman[1] gave for nitrogen, when changed into our units, are $A_0 = 1711.9$, a = 0.9338, $B_0 = 1.801$, b = —0.2466, $c = 1.5 \times 10.^6$ Their calculations were based on data from several sources, with the temperature range from -148.58 to 400° and with most of the pressures lying below 100 atmospheres, so their constants could hardly be expected to hold at high pressures.

It was not possible to fit satisfactorily all the A points in Fig. 2 with a straight line. However, they lie close to the parabola

$$A = 1528.6(1 - 0.2748/v - 0.9084/v^2) \qquad (4)$$

Introducing this parabola amounts to introducing a sixth parameter, a'; and

$$\left.\begin{array}{lll} A_0 = 1528.6 & a = 0.2748 & a' = 0.9084 \\ B_0 = 1.643 & b = -0.9235 & \\ c = 2.2 \times 10^6 & & \end{array}\right\} \qquad (5)$$

are the values that we have determined for the six constants. With ϕ, ψ and ΓT^2 from Equation 2, the equation

$$P_{\text{calcd.}} = \psi T - \Gamma - \phi \qquad (6)$$

gives the calculated pressure at a chosen temperature and volume. Table III lists the observed pressures and shows how the calculated pressures compare with them. A few of Bartlett's measurements for $v < 3$ are appended.

The agreement between observed pressures and those calculated both with the straight line and the parabola for A is remarkably good down to $v = 3$ cc. per g. over the entire temperature range. A study of the root mean square deviations shows that the parabola gives better agreement when the entire range of volume is considered—enough better to recommend the use of the six constants of Equation **5** rather than the five constants of Equation **3.**

One of the chief uses of an equation of state comes in thermodynamic calculations. There it is necessary that the equation represent trends accurately in order that the derivatives be reliable. From Fig. 2 it can be seen that the parabola follows the trend of the A points over the entire range of volume, whereas no straight line could do so. Further, the agreement between calculated and observed pressures for $v < 3$ (Table III) is also much better with the parabola; this shows that it still approximates the trend beyond the range of Fig. 2. So the behavior of nitrogen seems to be well represented by the six constants of Equation 5, for volumes down to 3 cc. per g. and from –70 to 400°. Calculations made with these constants should be fairly trustworthy over this range.

An examination of Table III shows that, while the equation of state seems satisfactory down to about $v = 3$ cc. per g., there is clearly something wrong when $v < 3$ at the low temperatures. There is no doubt that the addition of terms in $1/v^2$ for B and $1/v^3$ for A would effect an improvement, but this would bring in two more constants that are not needed when $v \geq 3$. The equation seems to have a definite limitation in the neighborhood of 3 cc. per g. at medium and low temperatures.

The data on hydrogen and its 3:1 mixture with nitrogen obtained by Bartlett and his collaborators is being similarly treated, and the results will appear shortly.

It is a pleasure to acknowledge our indebtedness to Dr. Oscar C. Bridgeman and Professor James A. Beattie, the authors of the equation of state, for many helpful suggestions. We have had the willing cooperation of Dr. Bartlett throughout the course of this work.

Summary

Bartlett has recently extended his P–V–T measurements on nitrogen to include ten temperatures in the interval –70 to 400°, up to 1000 atmospheres. His measurements and compilations cover a much greater range than has hitherto been embraced. It is now possible to subject an equation of state to a severe test and to ascertain its limitations. The writers find for nitrogen the values

$$A_0 = 1528.6 \qquad a = 0.2748 \qquad a' = 0.9084$$
$$B_0 = 1.643 \qquad b = -0.9235 \qquad c = 2.2 \times 10^6$$

in the units of grams, atmospheres, and cubic centimeters, for the constants in the Beattie–Bridgeman equation of state,

$$Pv^2 = rT\,[v + B_0\,(1 - b/v)]\,(1 - c/vT^3) - A_0\,(1 - a/v - a'/v^2)$$

r correspondingly expressed in cc. atm. per g. per degree. In this investigation a method of curve-fitting has been used that accurately reproduces trends as well as actual pressures in the P–V–T relations. With the constants given above, over the temperature range –70 to 400° the equation reproduces pressures with a root mean square deviation of 0.50% at 4 cc. per g., the maximum being 0.95%; and with a root mean square deviation of 0.78% at 3 cc. per g., the maximum deviation being 1.41%. Thus the equation with the above constants reproduces trends and pressures satisfactorily from –70 to 400° down to 3 cc. per g. Below 3 cc. per g. the calculated pressures are invariably too low, and the discrepancy becomes very large at low temperatures and low volumes.

WASHINGTON, D. C.

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

THE ACTIVITY COEFFICIENT OF SILVER ACETATE

BY F. H. MACDOUGALL

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The activity coefficient of silver acetate was determined by means of measurements of the solubility of the salt in water and in aqueous solutions of potassium nitrate. Of the chief materials used in this investigation, the water was "conductivity" water obtained by distilling ordinary distilled water after the addition of sodium hydroxide and potassium permanganate in a tin-lined copper vessel; the potassium nitrate was Baker's "Analyzed" and was dried at 150° for several hours before using; and the silver acetate was from Mallinckrodt and gave on analysis 64.64, 64.55 and 64.59% of silver compared with 64.64% calculated from the formula.

The solutions of potassium nitrate were prepared by weighing out the water and the salt and were then put into glass-stoppered amber-colored bottles containing an excess of silver acetate. The stoppers were heavily paraffined and the bottles were then rotated in a water-bath at 25.00 ∓ 0.03° for at least seven or eight hours and frequently for twenty-four hours or more.

The saturated solution in a bottle was then examined in the following way: while the bottle was still almost completely immersed in the bath, the stopper was removed and a glass tube with the lower end wrapped in absorbent cotton was inserted. The cotton was tied to the tube by means of platinum wire. By applying suction to the tube approximately 50 cc. of the solution (which originally amounted to about 100 cc.) was transferred to a glass vessel which was now immersed fairly completely in the water-bath. After some minutes two separate portions of about 25 cc. each were withdrawn by means of an accurately calibrated pipet and transferred to weighing bottles. After being weighed, the solutions were washed into 400-cc. beakers, a few drops of nitric acid added, the solutions heated to boiling and then dilute hydrochloric acid was added until there was a slight excess. The beakers were set aside for a number of hours, usually overnight, and then the mixture was filtered using Gooch crucibles. These were then dried in an oven at 150° to constant weight. From the weight of solution delivered by the pipet, the density of the solution was obtained with an accuracy of at least 1 part in 2000. At least two independent experiments were made for each concentration of potassium nitrate, and analyses were made on two separate samples of the solution from each bottle.

Methods of Expressing Composition of Solution.—The composition of the solution saturated with silver acetate is expressed in several ways: first, by giving the molality, m, or moles of silver acetate per 1000 g. of water; second, by giving the molarity, c, or moles per liter of solution, and, third, by giving the mole fraction, x, of Ag^+ or acetate ion, assuming that the silver acetate and the potassium nitrate are completely ionized and taking **18.015** as the molecular weight of water. In addition, I have introduced the term "normalized mole fraction," $|x|$, which, for aqueous solutions, is defined by the equation, $|x| = 55.51x$. The advantage arising from the use of this term is that for a given solution the normalized mole fraction is approximately equal to the molarity or the molality.

In Table I is given a summary of the determinations of the solubility of silver acetate in water at 25°.

TABLE I

SOLUBILITY OF SILVER ACETATE IN WATER AT 25°

Author	Year	G. per liter of soln.	Author	Year	G. per liter of soln.
Raupenstrausch[1]	1885	11.21	Hill and Simmons[4]	1909	11.13
Goldschmidt[2]	1898	11.16	Knox and Wills	1919	11.13
Jaques[3]	1909	11.07	MacDougall	1929	11.09

Table II gives the solubility of silver acetate in aqueous solutions of potassium nitrate in which the molality of the potassium nitrate ranges from 0 to 3. It will be noted that the solubility of silver acetate expressed as molarity has reached a maximum for a molality of potassium nitrate of

TABLE II

SOLUBILITY OF SILVER ACETATE IN PRESENCE OF POTASSIUM NITRATE

m = molality; c = molarity, x = mole fraction × 55.51

m, KNO_3	d of satd. soln.	m, AgOAc	c, AgOAc	x, AgOAc
0	1.0047	0.06685	0.06642	0.06669
0.05009	1.0077	.07041	.06978	.07011
.1006	1.0115	.07281	.07204	.07236
.2001	1.0180	.07659	.07547	.07584
.3018	1.0241	.07941	.07791	.07833
.4010	1.0298	.08171	.07982	.08031
.5013	1.0366	.08344	.08124	.08171
.6040	1.0417	.08498	.08233	.08292
.8021	1.0537	.08786	.08449	.08513
1.0155	1.0658	.09019	.08600	.08673
1.2431	1.0784	.09214	.08708	.08791
1.5437	1.0944	.09453	.08828	.08926
2.0371	1.1186	.09750	.08923	.09054
2.5355	1.1426	.09997	.08973	.09130
3.0139	1.1653	.10163	.08960	.09137

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[1] Raupenstrauch, *Monatsh.*, **6**, 563 (1885).

[2] Goldschmidt, *Z. physik. Chem.*, 25, 91 (1898).

[3] Jaques, *Trans. Faraday Soc.*, *5*, 225 (1909).

[4] Hill and Simmons, THIS JOURNAL, 31, 821 (1909); *Z. physik. Chem.*, *67*, 594 (1909).

[5] Knox and Will, J. *Chem. Soc.*, 115,853 (1919).

about 2.5, that expressed as mole fraction the maximum solubility occurs at a molality of potassium nitrate of about 3 and that expressed as molality the maximum solubility has not been attained in these experiments.

Discussion of Experimental Results

On the basis of the theory of Debye we may write

$$-\log_{10} f = \log_{10} x - \log_{10} x_0 = \frac{0.5045\, S^{1/2}}{1 + 0.3283 \times 10^8\, aS^{1/2}} = \frac{0.5045\, S^{1/2}}{1 + AS^{1/2}} \qquad \text{(I)}$$

where f is the mean activity coefficient of silver and acetate ions in the saturated solution or, more briefly, the activity coefficient of silver acetate $S_c = \Sigma C_i Z_i^2/2$ is the ionic strength of the solution in which an ion of the i-th kind has a valence of z_i and a molarity, C_i; a is an "average" diameter to be assigned to the silver and acetate ions in the solutions investigated, and x is the "normalized" mole fraction of either silver or acetate ions. We may interpret x_0 as the value of x which would be obtained for a saturated solution of silver acetate in case the silver and acetate ions were ideal; or in terms of the Debye equation, x_0 is the value of x extrapolated to a solution of zero ionic strength. Corresponding to x_0 there will be a value m_0 and a value c_0, defining thus three activity coefficients, *viz.*

$$f = \frac{x_0}{x} \qquad \gamma = \frac{m_0}{m} \qquad \gamma_c = \frac{c_0}{c} \qquad \text{(II)}$$

From two sets of corresponding values of x and S_c, it is possible, using Equation I, to find a value of x_0 and a value of A (or a). Table III contains the values of A and x_0, obtained using in every case the values of x and S_c for $m = 0$ with respect to potassium nitrate combined successively with the values of x and S_c for each of the solutions containing potassium nitrate.

TABLE III

A AND x_0 FROM $m_{KNO_3} = 0$ AND THE VALUE OF m_{KNO_3} IN FIRST COLUMN

m, KNO_3	S_c	A	x_0	m, KNO_3	S_c	A	x_0
0.05009	0.1194	1.4274	0.05358	0.8021	0.8558	1.4120	0.05355
.1006	.1715	1.4789	.05369	1.0155	1.0543	1.4405	.05361
.2001	.2727	1.4297	.05359	1.2431	1.2619	1.4625	.05366
.3018	.3740	1.4493	.05363	1.5437	1.5300	1.4763	.05369
.4010	.4716	1.4079	.05354	2.0371	1.9535	1.5138	.05376
.5013	.5694	1.4266	.05358	2.5355	2.3655	1.5497	.05384
.6040	.6675	1.4388	.05360	3.0139	2.7469	1.6021	.05396

It will be evident from Table III that up to an ionic strength of at least unity the values of A are sensibly constant but that above this ionic strength the values of A obtained exhibit an upward drift. The mean of the first ten values of A is 1.4311, which does not differ appreciably from the third value of the table (1.4297). The latter value of A and the corresponding value of x_0, *viz.*, 0.05359, were used in the following calculations. From $A = 1.430$, we have $a = 4.35 \times 10^{-8}$ cm. The extrapolated density of the solution corresponding to $x_0 = 0.05359$ is 1.0032. Moreover, we find from this value of x_0 and the density $m_0 = 0.05369$, $C_0 = 0.05338$. Table IV contains the observed values of x and the values of x calculated by Equation I. It will be seen that this equation gives excellent results up to an ionic strength of greater than one.

Finally, I give in Table V, the observed activity coefficients of silver acetate based on the values x_0, m_0 and c_0 already obtained.

By adding to the right-hand side of Equation I a term proportional to the ionic strength, it is possible to obtain an expression which will reproduce the experimental results even in the high ionic strengths. This point will not be discussed further in this paper.

TABLE IV

OBSERVED AND CALCULATED VALUES OF x WITH $A = 1.430$ AND $x_0 = 0.05359$

S_0	x, obs.	x, calcd.	S_0	x, obs.	x, calcd.
0.06642	0.06669	0.06669	0.8558	0.08513	0.08492
.1194	.07011	.07010	1.0543	.08673	.08688
.1715	.07236	.07249	1.2619	.08791	.08841
.2727	.07584	.07584	1.5300	.08926	.09004
.3740	.07833	.07828	1.9535	.09054	.09209
.4716	.08031	.08014	2.3655	.09130	.09367
.5694	.08171	.08169	2.7469	.09137	.09488
.6675	.08292	.08301			

TABLE V

ACTIVITY COEFFICIENT OF SILVER ACETATE AT 25° IN SOLUTIONS OF POTASSIUM NITRATE

S_0 Ionic strength	f	γ	γ_c	S_0 Ionic strength	f	γ	γ_c
0.06642	0.804	0.803	0.804	0.8558	0.629	0.611	0.632
.1194	.764	.763	.765	1.0543	.618	.595	.621
.1715	.741	.737	.741	1.2619	.610	.583	.613
.2727	.707	.701	.707	1.5300	.600	.568	.605
.3740	.684	.676	.685	1.954	.592	.551	.598
.4716	.667	.657	.669	2.366	.587	.537	.595
.5694	.656	.644	.657	2.747	.586	.528	.596
.6675	.646	.632	.648				

Summary

Measurements have been made of the solubility at 25° of silver acetate in water and in aqueous solutions of potassium nitrate up to a molality of 3.014. The Debye expression for the activity coefficient using an ionic diameter of 4.35×10^{-8} cm. represents the experimental facts up to an ionic strength of over one. The activity coefficients of silver acetate in the various solutions are presented in tabular form.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF COPENHAGEN]

THE KINETIC DETERMINATION OF HYDROGEN-ION CONCENTRATIONS IN AQUEOUS SOLUTION

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1. Introduction

The principles of the various methods which have served for the determination of the concentration of hydrogen ions in aqueous solutions were originally developed with only slight consideration of the phenomenon known as "salt effect." However, as early as 1887 Arrhenius[2] showed that kinetic reactions were influenced by the presence of neutral salts. In his fundamental investigations on the measurement of hydrogen-ion concentrations and their significance in biochemical reactions, Sørensen[3] called attention to the effects of salts in the colorimetric and the kinetic methods, while the electrometric method was generally adopted as a standard method in which such influences were supposed to be absent. It was later realized as a consequence of the more recent aspects of the theory of salt solutions that electrometric measurements also are considerably affected by the presence of salts, but up to the present time the electrometric method seems still to be generally considered as the most reliable and the most suitable method for accurate determinations of hydrogen-ion concentration. Even if this be true in some cases, it should be noted that salt effects manifest themselves in a much simpler way in a catalytic reaction than in either electrometric or colorimetric determinations, and that, from this point of view, since salt effects form one of the most serious sources of error in hydrogen-ion measurements, the kinetic method stands out as marked by considerable advantages.

The most rational method for the elimination of the errors to which these salt effects may lead is, obviously, to compare by the method adopted the solution under examination with a reference solution of which the hydrogen-ion concentration is known from the stoichiometric amount of completely ionized acid present and which exhibits as nearly as possible the same medium effect as the solution of unknown hydrogen-ion concentration. Kinetic methods based on this principle have rendered particularly satisfactory service in the determination of the acidity of a number of aquo-ions.[4] However, it has not always been easy to prepare a reference solution which as regards its medium effect is sufficiently close to the test solution. Hence, in addition to throwing light on the general

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[1] Fellow of the American-Scandinavian Foundation, 1928–1929.

[2] Arrhenius, *Z. physik. Chem.*, **1**, 110 (1887).

[3] Sørensen, *Medd. från Carlsberg lab.*, *8*, 1 (1910).

[4] Bronsted and Volquartz, *Z. physik. Chem.*, **134**, 97 (1928).

kinetics of the effects of salts, an extensive examination of all these phenomena should contribute considerably to the problem of accurate hydrogen-ion determination.

For the solution of this problem it is, of course, very important to possess a number of suitable catalytic reactions of varied sensitivity which may be subject to accurate and easy experimental examination. As a result of extensive experimental investigations, Skrabal[5] and his co-workers have recently brought to light a large number of catalytic reactions many of which seem very useful for this purpose. It has also been shown[6] that several of these reactions can be investigated by a simple dilatometric method.

In using the catalytic method for the determination of hydrogen-ion concentrations, there is, however, a point which requires special consideration. According to a recent extension of the theory of acid and basic catalysis,' the catalysis by hydrogen ion—which is actually not the free proton, but a chemical compound H_3O^+—is to be looked upon only as a special case of general acid catalysis. If the solution in which the concentration of hydrogen ion is to be determined contains acids other than H_3O^+, the catalytic action exhibited by the solution may be a compound effect in which all the acids present take part. Also the solvent itself by virtue of its acid–basic character may be catalytically active. The catalytic relations involved in such cases seem to be of a certain simplicity and are discussed elsewhere. However, for the exact determination of hydrogen-ion concentrations, it is preferable that those catalytic reactions be selected in which general acid–basic effects of this kind are absent or are at least proved to be negligible as compared with the effect of the hydrogen ion itself. Fortunately, there seems to be no difficulty in finding reactions which fulfil these simple conditions.

In the above-mentioned paper by Bronsted and Wynne-Jones[6] the use of diethyl acetal and similar compounds was suggested as a means of determining hydrogen-ion concentrations. With a view to making a further investigation of hydrolytic reactions and of their use in the determination of hydrogen ions at fairly high concentrations, with particular reference to the effect of salts, we have in the present study investigated the hydrolytic reactions of several acetals less sensitive to hydrogen ions than diethyl acetal.

2. The Reactants and their Preparations

Skrabal,[5] reviewing the extensive work of himself and his co-workers on the hydrolytic reactions of esters, acetals, etc., states that, in general, for a given aldehyde, the sensitivity of the corresponding acetals to hydrogen-ion catalysis of hydrolysis increases with the complexity of the

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

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

[7] Bronsted, *ibid.*, **24,** 63 (1928).

alcohol involved and that, conversely, for a given alcohol, the sensitivity of its acetals increases with the complexity of the aldehyde used in their preparation. Skrabal and Sawiuk,[8] on the basis of roughly quantitative measurements, give tables for the relative rates of hydrolysis as the numbers of carbon atoms in the alcohol chain and in the aldehyde chain are increased. From these tables it appears that the acetal of methyl alcohol should give a convenient velocity of hydrolysis in the hydrogen-ion range around 0.001 to 0.005 equivalent per liter and that dimethyl isobutyral should cover a slightly higher range. Accordingly, these substances were prepared and tested.

Dimethyl acetal was prepared from methyl alcohol and 95% acetaldehyde by the method suggested by Adkins and Nissen[9] using calcium chloride as a catalytic dehydrating agent.

Twenty grams of anhydrous neutral calcium chloride was dissolved in seventy grams of methyl alcohol in a stout 250-cc. bottle with a tightly-fitting glass stopper. After thoroughly cooling in an ice-bath, fifty cc. of 95% acetaldehyde was poured carefully down the side of the bottle so as to form a separate layer. The bottle was then tightly stoppered and thoroughly shaken. A reaction, resulting in a considerable evolution of heat, took place immediately. The bottle was shaken overnight in a continuous shaker to complete the reaction. Upon standing in a separatory funnel for a few minutes, the acetal rose to form a light separate layer and was separated from the salt solution. It was washed several times with concentrated calcium choride solution and once with water. It then stood for several hours, during which time considerable water separated. The pure acetal was decanted from the water and was then dried over anhydrous potassium carbonate and purified by fractional distillation through an efficient column. The product used boiled at 63.5 to 64.5° (uncorrected).

Carrying Skrabal's ideas as to decreasing sensitivity with decreasing complexity a step further, the acetal of ethylene glycol should be even less sensitive to H_3O^+ catalysis of hydrolysis than is dimethyl acetal, even though the difference of but two hydrogen atoms may be rather slight.

This acetal, otherwise known as ethylene ethylidene oxide, was prepared in a manner similar to that used for the preparation of dimethyl acetal, also using calcium chloride as catalyst. Since it shows a high reciprocal solubility with water, it was washed only with concentrated calcium chloride solution three or four times. Most of the water was removed by allowing the acetal to stand for some time over anhydrous calcium chloride, after which the drying was completed over anhydrous potassium carbonate. After purification by fractional distillation, the acetal boiled at 82.5 to 83° (uncorrected).

3. Experimental Method

As the hydrolysis of the acetals here dealt with is accompanied by a considerable volume change, expansion in the case of dimethyl acetal

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[8] Skrabal and Sawiuk, Z. *physik. Chem.*, 122, 357 (1926).

[9] Adkins and Nissen, THIS JOURNAL, **44, 2749** (1922).

and of dimethyl isobutyral and contraction in the case of ethylene acetal, the course of the reaction may be followed by the dilatometric method used by Bronsted and Wynne-Jones.[6] In fact, the same dilatometers were used, one having a bulb holding 115 cc. and a capillary with a cross section of 0.32 mm. and the other a bulb holding 165 cc. and a capillary with a cross section of 0.13 mm. A calibration of these capillaries showed a uniformity of cross section within 1%. A convenient volume change was obtained with an acetal concentration of 0.01 to 0.04 molal.

The dilatometers were placed in electrically heated and controlled water thermostats maintained at 20 ± 0.01°.

The velocities of reaction were calculated by the method described by Guggenheim,[10] and are expressed as $k = -d \ln c/dt$ in min.$^{-1}$ using natural logarithms.

4. Standardization of Acetals

The first work undertaken was the verification of the strict dependence of the velocity of hydrolysis upon the H_3O^+ concentration in solutions of strong acids. To this end, the velocity of hydrolysis of dimethyl acetal was measured in solutions of perchloric acid ranging from 0.001 to 0.005 molar, and the constant $k_{H_3O^+}$ for molal acid calculated therefrom.

As will be seen from the constancy of $k_{H_3O^+}$ and from Fig. 1, there is a straight line relationship between the velocity of hydrolysis and the H_3O^+ concentration of the hydrolyzing medium. Since the concentrations are so low, no detectable salt effect due to the acid can be expected.

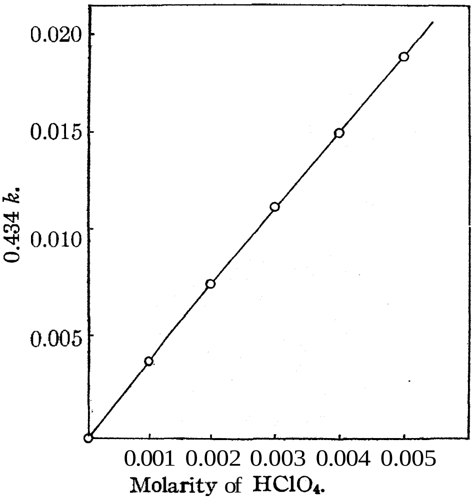

Fig. 1.—The hydrolysis of dimethyl acetal in perchloric acid solutions ($t = 20°$).

The work on dimethyl *iso*butyral never passed the preliminary stage, since it was found to cover approximately the same range of H_3O^+ concentrations as the more readily obtainable dimethyl acetal. Preliminary experiments showed the following results for the hydrolysis in solutions of perchloric acid.

It is apparent that for a given H_3O^+-concentration the *iso*butyral hydrolyzed about 1.1 times as rapidly as the corresponding acetal. Skrabal and Sawiuk reported 0.69 for the same ratio.

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[10] Guggenheim, *Phil. Mag.*, 1, 538 (1926).

TABLE I

HYDROLYSIS OF DIMETHYL ACETAL

Molarity of $HClO_4$....	0.001	0.001	0.002	0.002	0.003	0.003
$0.434\ k \times 10^3$........	3.91	3.98	7.77	7.86	11.82	11.76
$0.434\ k_{H_3O^+}$..........	3.91	3.98	3.89	3.93	3.94	3.92
Molarity of $HClO_4$....	0.004	0.004	0.005	0.005		
$0.434\ k \times 10^3$........	15.67	15.94	19.31	19.37		
$0.434\ k_{H_3O^+}$..........	3.92	3.90	3.86	3.87	Mean value, 3.92	

TABLE II

HYDROLYSIS OF DIMETHYLISOBUTYRAL

Molarity of $HClO_4$......................	0.003	0.004
$0.434\ k \times 10^3$.........................	12.7	17.7
$0.434\ k_{H_3O^+}$...........................	4.22	4.42

In the case of the ethylene acetal, the hydrolysis is so insensitive to hydrogen ions that—at reasonable velocities—the concentration of the acid in the hydrolyzing medium may have an appreciable salt effect. In fact, this effect is quite noticeable and the curve showing the relationship of the velocity constant of hydrolysis to the H_3O^+ concentration, instead of being a straight line, is convex downward as shown by Fig. 2. The velocities of hydrolysis of ethylene acetal in solutions of perchloric acid are as follows.

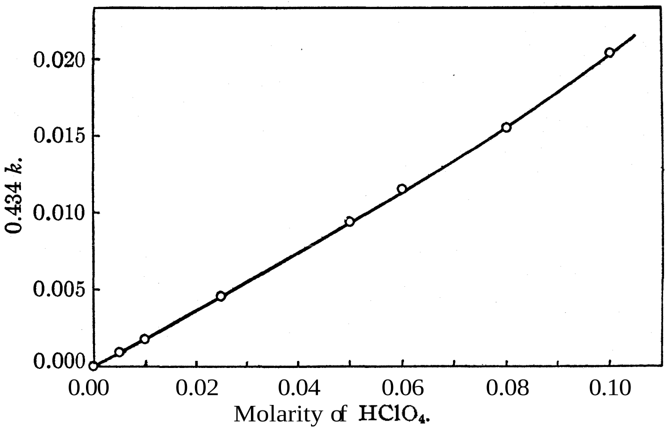

Fig. 2.—Velocity of hydrolysis of ethylene acetal in perchloric acid solutions (t = 20°).

TABLE III

HYDROLYSIS OF ETHYLENE ACETAL

Molarity of $HClO_4$...........	0.005	0.010	0.025	0.050 (HCl)	0.050
$0.434\ k \times 10^3$...............	0.912	1.82	4.62	9.35	9.40
$0.434\ k_{H_3O^+}$...................	0.182	0.182	0.185	0.187	0.188
Molarity of $HClO_4$...........	0.060	0.080	0.100	0.100	0.100
$0.434\ k \times 10^3$...............	11.50	15.58	20.3	20.4	20.2
$0.434\ k_{H_3O^+}$...................	0.192	0.195	0.203	0.204	0.202

That the increase in the velocity constant is a linear salt effect is shown in Fig. **3** by the straight line relationship of $k_{H_3O^+}$ to the H_3O^+ concentrations. The molar velocity constant for the catalytic hydrolysis of ethylene acetal is given by the equation

$$0.434\, k_{H_3O^+} = 0.180 + 0.19c$$

where c is the concentration of the acid producing the salt effect.

5. Absence of Acid Catalysis

As already pointed out, if one proposes to use the rate of reaction as a measure of the H_3O^+-concentration, troublesome complications are introduced if there are present in the solution under examination substances which have a similar catalytic effect large enough to be apparent above the limit of experimental error. It is important, therefore, to ascertain whether such a general acid effect is present in the reaction studied or not.

It was previously found by Bronsted and Wynne-Jones that diethyl acetal shows no general acid catalysis. It is probable, therefore, that such an effect is also absent in the hydrolysis of dimethyl acetal. Furthermore, it has been shown, in connection with the generalized theory of acid and basic catalysis, that in order to show a detectable catalysis by acids in general, a reaction catalyzed by H_3O^+ ions must also have a detectable "spontaneous" reaction. Hence the absence of a detectable "spontaneous" reaction of hydrolysis of these acetals should indicate the absence of any detectable acid catalysis.

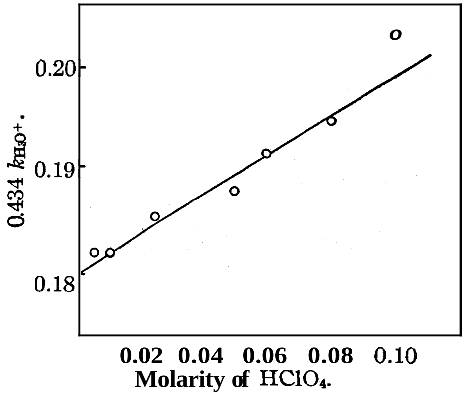

Fig. 3.—Salt effect of perchloric acid upon the hydrolysis of ethylene acetal (t = 20°).

In order to detect any possible spontaneous reaction, 0.08 molal solutions of the acetals in distilled water neutral to brom thymol blue were prepared and placed each in a sealed dilatometer, being allowed to stand in the thermostat at 20° for forty-five days. At the end of that time, in each dilatometer, the meniscus was, within the error of reading, in its original position, indicating the absence of any spontaneous reaction with a velocity constant above 5×10^{-8} and the probable absence of any detectable "acid catalysis."

This conclusion was corroborated by other experiments. The dimethyl acetal was allowed to hydrolyze in solutions 0.00294 molar in perchloric acid and containing different amounts of the weak acid phenol. These results are as follows.

TABLE IV

HYDROLYSIS OF DIMETHYL ACETAL IN THE PRESENCE OF PHENOL

Molarity of phenol	0.00	0.10	0.20
0.434 *k*	0.01160	0.01154	0.01156

Even if a slight catalytic effect of the phenol may have been masked by a simultaneous counteracting medium effect, the conclusion that there is no detectable general acid catalysis in the hydrolysis of dimethyl acetal seems well justified.

It was somewhat more difficult to show the absence of general acid catalysis of ethylene acetal because of the difficulty of obtaining a buffered solution giving a suitable hydrogen-ion concentration or of finding a weak acid whose dissociation in a solution of perchloric acid of suitable strength would give *a* definitely known hydrogen-ion concentration. The second method was finally adopted and acetic and monochloro-acetic acids, whose dissociation constants are rather definitely known, were used as the weak acids to be added to the solutions of perchloric acid used as a hydrolyzing medium. From the dissociation constants of these weak acids, the H_3O^+ concentrations of the solutions used were calculated with an accuracy comparable with that of the experiment.

In calculating from the dissociation constant of a weak acid the H_3O^+ concentration of a solution containing definite amounts of a weakly and of a completely ionized acid, the ionization of the weaker will be repressed by the H_3O^+ of the stronger to such an extent that it will furnish only a small part of the H_3O^+ present. Hence, although it is necessary to make an approximation in determining the value of the dissociation constant of the weak acid in the particular solution being used, any slight uncertainty in this estimation will cause only a very small percentage error in the calculated value of the total H_3O^+ concentration to be measured. This method was used in calculating the H_3O^+ concentrations given in the second column of Table V as those to be expected if there is no general acid catalysis. The velocity constant corresponding to this H_3O^+ concentration (taken from Table III) was then compared with that found with the following results.

TABLE V

HYDROLYSIS OF ETHYLENE ACETAL IN VARIOUS ACID MIXTURES

Concn. of acids		Calcd. H_3O^+	Corresponding k	k Found
0.05 $HClO_4$	0.10 $ClCH_2COOH$	0.0545	0.01030	0.01033
0.05 $HClO_4$	0.20 CH_3COOH	.0505	.00951	.00950
0.075 $HClO_4$	0.10 $ClCH_2COOH$	.0787	.01525	.01533

From these results it is apparent that there is no general acid catalysis of the hydrolysis of ethylene acetal great enough to be shown above the limit of experimental error of these experiments. Thus we may conclude that the velocities of hydrolysis of these two acetals are, in the absence of salts, dependent only upon the H_3O^+ concentrations of the hydrolyzing media.

6. Salt Effects

The hydrolytic reactions of the acetals are particularly suitable for a study of primary salt effects, since the reactions are sufficiently insensitive to hydrogen ion to be measured in solutions in which the acidity is well defined by the presence of strong acids only. The study of the primary salt effect may, therefore, be carried out in solutions containing no weak electrolytes and the complications introduced by a concurrent secondary salt effect are avoided.

The results of a series of experiments on the effects of various salts upon the velocity of hydrolysis of dimethyl acetal in perchloric acid solutions are given in Table VI. The velocities found for the salt solutions are given as decimal fractions of that found in the presence of the same concentration of pure perchloric acid with no salt present. The experiments were made at various H_3O^+ concentrations. In a number of cases, the recorded values are the average of several concordant experimental results.

TABLE VI

SALT EFFECT UPON THE HYDROLYSIS OF DIMETHYL ACETAL

	Salts[a]	Equivalent concentration 0.05	0 10	0.15	0.20	0.30
1	NaCl	1.058	1.123	...	1.235	...
2	$NaClO_4$	...	1.133	...	1.27	...
3	$NaNO_3$	...	1.092	...	1.175	...
4	$NaOC_6H_2(NO_2)_3$	0.992	0.980	0.974	...	...
5	$NaSO_3C_2H_5$	1.023	1.060	1.093	1.133	1.196
6	$NaSO_3C_6H_5$	1.041	1.070	...	1.140	1.195
7	$NaSO_3C_{10}H_7$	1020	1043	1.084	1.110	...
8	KNO_3	...	1.100	...	1.180	...
9	NH_4Cl	...	1.110	...	1.200	...
10	$BaCl_2$	1.082	1.193	...	...	...

[a] Salt 4 is picrate, No. 5 is ethyl sulfonate and No. 7 is naphthalenesulfonate.

In the case of ethylene acetal, the salt effect was determined only for sodium perchlorate and sodium nitrate, all measurements being made at a perchloric acid concentration of 0.05 M; the acid concentration was kept constant in this case since it is large enough itself to exhibit a considerable salt effect. The figures in Table VII are, as before, the ratio of the velocities in the salt-containing solutions to that in a solution 0.05 *M* in perchloric acid and containing no salt.

TABLE VII

SALT EFFECT UPON THE HYDROLYSIS OF ETHYLENE ACETAL

	Salt	Equivalent concentration 0.05	0.10	0.15	0.20
1	$NaClO_4$	...	1.165	1.239	1.326
2	$NaNO_3$	1.039	1 080	1.123	1.172

These results are illustrated graphically by Fig. 4 and Fig. 5. It will readily be seen that, for these two acetals, the increase in velocity of hydrolysis in the presence of increasingly large amounts of salt is, up to a salt concentration of 0.2 M, directly proportional to the concentration of the salt. The individual nature of the salt has, however, a very great influence; for instance, sodium perchlorate in the hydrolysis of dimethyl acetal shows an effect two to three times as great as that of the least effective salt, sodium naphthalenesulfonate. The negative values recorded[*] for sodium picrate are undoubtedly due to the incomplete dissociation of picric acid and are not to be looked upon as a real primary effect. However, the dissociation constant of picric acid cannot be calculated from these data since the actual salt effect of the picrate is unknown.

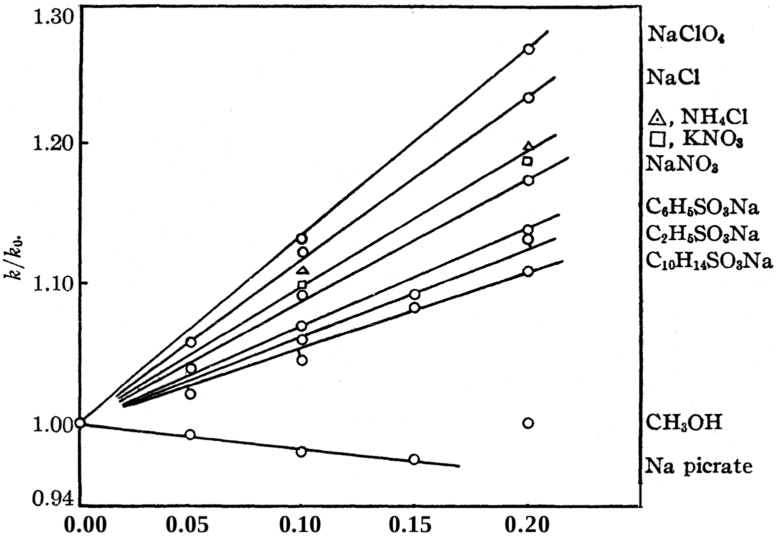

Fig. 4.—The primary salt effects upon the catalytic hydrolysis of dimethyl acetal (t = 20°).

It will be seen from Tables III and VII and from Figs. 3 and 5 that the salt effect of perchloric acid upon the hydrolysis of ethylene acetal is lower than the effect of sodium perchlorate. Methyl alcohol at a concentration of 0.20 M showed no measurable effect upon the hydrolysis of dimethyl acetal.

For the general applicability of the reactions here studied, the considerable salt effect demonstrated above is, of course, a complicating factor, unless the salt concentration is below 0.01 or the identity and concentration of any salts present are known. In many reactions, as for instance the inversion of cane sugar and the mutarotation of glucose, the salt effect is much smaller. It is to be hoped that reactions may be found which will combine insensitiveness to salts with the marked practical advantages of the reactions studied in the present investigation.

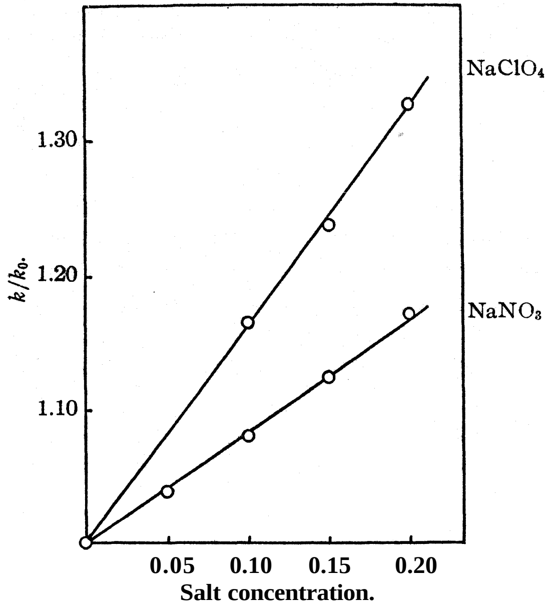

Fig. 5.—Salt effect on the hydrolysis of ethylene acetal (t = 20°).

Appreciation.—The authors wish to express to the American–Scandinavian Foundation their sincere gratitude for and appreciation of the grant of a fellowship to the junior author, making possible his coöperation in this research.

7. Summary

1. Dimethyl acetal and ethylene acetal have been prepared and their velocities of hydrolysis have been measured in solutions of perchloric acid at different concentrations. The velocity of hydrolysis is found to be directly proportional to the H_3O^+ concentration of the hydrolyzing medium. It is proposed to use the hydrolysis of these acetals for the measurement of hydrogen-ion concentrations.

2. It has been shown that these hydrolyses are not catalyzed to a detectable extent by acids other than H_3O^+.

3. The primary salt effect of various salts upon the catalytic hydrolyses of these acetals has been studied and is shown to be, up to a salt concentration of 0.2 M, a linear function of the concentration.

4. The magnitude of the primary salt effect is largely a function of the individual nature of the salt.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF COPENHAGEN]

THE DISSOCIATION OF MONOCHLORO-ACETIC ACID IN AQUEOUS SOLUTION

BY CLINTON GROVE[1]

RECEIVED NOVEMBER 30, 1929 PUBLISHED APRIL 7, 1930

The determination of H_3O^+ concentrations by the catalytic hydrolysis of dimethyl acetal and of ethylene acetal as proposed by Bronsted and Grove[2] is particularly useful in the determination of H_3O^+ concentrations in solutions of pure weak acids where there is only a small ionic concentration and consequently practically no salt effect upon the hydrolytic reaction. From such measurements, of course, the dissociation constant of the acid is readily calculated. The velocity of hydrolysis of the acetal—a linear function of the H_3O^+ concentration—is readily determined by a simple dilatometric method.

In the present work this method has been applied to the determination of the H_3O^+ concentrations of solutions of monochloro-acetic acid from 0.003 to 0.30 molar.

Theoretical

In an aqueous solution of any weak acid, HA, the following equilibrium is found to obtain

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

The classical mass action expression for this equilibrium is given by

$$K_c = \frac{c_{A^-} \cdot c_{H_3O^+}}{c_{HA} \cdot c_{H_2O}} \qquad (1)$$

where the c's are the concentrations of the respective ions and compounds. This quantity K_c, however, is not a true constant but varies with the ionic strength. If the ionic concentrations be replaced by their respective activities, the resulting expression

$$K_a = \frac{a_{A^-} \cdot a_{H_3O^+}}{a_{HA} \cdot a_{H_2O}} \qquad (2)$$

shows a quantity K_a which is a true constant, independent of the ionic strength. From the fundamental equation for the activity

$$a = cf \qquad (3)$$

where f is the activity coefficient, we arrive at the following equation which relates K_c to K_a

$$K_a = \frac{a_{A^-} \cdot a_{H_3O^+}}{a_{HA} \cdot a_{H_2O}} = \frac{c_{A^-} \cdot c_{H_2O^+}}{c_{HA} \cdot c_{H_2O}} \cdot \frac{f_{A^-} \cdot f_{H_3O^+}}{f_{HA} \cdot f_{H_2O}} = K_c \cdot \frac{f_{A^-} \cdot f_{H_3O^+}}{f_{HA} \cdot f_{H_2O}} \qquad (4)$$

Applying the Debye–Hückel expression for the change in activity coefficient with the ionic strength

$$-\log f = \alpha z\sqrt[2]{\mu} + \beta\mu \qquad (5)$$

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[1] Fellow of the American–Scandinavian Foundation, 1928–1929.

[2] Brönsted and Grove, THIS JOURNAL, 52, 1394 (1930).

where z is the valence, μ the ionic strength and α and β are constants, to Equation 4, we arrive at an expression for the variation of the classical "constant" with the ionic strength

$$\log K_c = \log K_a - z_A \sqrt{\mu} - \beta\mu \tag{6}$$

For an electrolyte which on dissociation produces a univalent negative ion along with the hydroxonium ion, Equation 6 assumes the form

$$\log K_c = \log K_a + \sqrt{\mu} - \beta\mu \tag{7}$$

Experimental

The solutions of monochloro-acetic acid were prepared by weighing out rapidly the necessary quantities of pure monochloro-acetic acid which had been recrystallized from benzene and dried *in vacuo* over sulfuric acid, and dissolving in distilled water. Solutions could be prepared in this manner to within 1% of the desired concentration, the solutions later being adjusted to the exact strength desired. The stock solutions were standardized against a solution of sodium hydroxide of accurately known titer. The solutions used were made up by dilution of these stock solutions immediately before the experiments were made.

The velocities of hydrolysis at acid concentrations of **0.003** to **0.015** molar were determined by the use of dimethyl acetal and the H_3O^+ concentrations were calculated from the expression given by Bronsted and Grove for the relation of the velocity of hydrolysis to the H_3O^+ concentration

$$0.434\, k_{H_3O^+} = 3.92 \text{ or } c_{H_3O^+} = 0.434\, k/3.92$$

At acid concentrations from **0.05** to **0.30** molar, the velocities of hydrolysis were determined by the use of ethylene acetal and the H_3O^+ concentrations

TABLE I

RESULTS OF EXPERIMENTS

c_{ClCH_2COOH}	$c_{H_3O^+}$	$\sqrt{\mu}$	$K_c \times 10^3$	Log K_c
0.003	0.00151	0.0388	1.53	7.185–10
	.00151		1.53	7.185–10
.005	.00212	.0460	1.56	7.193–10
	.00211		1.54	7.188–10
.010	.00327	.0567	1.58	7.193–10
	.00325		1.56	7.199–10
.015	.00416	.0646	1.59	7.201–10
	.00417		1.60	7.204–10
.050	.00823	.0908	1.62	7.210–10
	.00823		1.62	7.210–10
.100	.0120	.110	1.64	7.215–10
	.0121		1.66	7.220–10
.200	.0175	.132	1.68	7.225–10
	.0174		1.67	7.223–10
.300	.0217	.147	1.69	7.228–10
	.0216		1.68	7.225–10

were calculated from the expression for the catalytic hydrolysis of this acetal

$$c_{\mathrm{H_3O^+}} = 0.434\,k/0.180 + 0.19\,c_{\mathrm{H_3O^+}}$$

The results of these experiments are given in Table I.

The only other results with which these may be compared are those given in Table II, determined by Ostwald[3] using a conductivity method employing platinized electrodes which, he states, caused some alteration of the acid; and those given in Table III, determined by van't Hoff and Reicher,[4] who avoided alteration of the acid by the use of bright platinum electrodes but whose results are, nevertheless, less consistent than those of Ostwald. Since these measurements were interpreted in the classical way by

TABLE II

DATA OF OSTWALD

$c_{\mathrm{HlCH_2COOH}}$	K_c	$c_{\mathrm{ClCH_2COOH}}$	K_c
0.0625	0.00155	0.0039	0.00146
.0312	.00155	.0020	.00147
.0156	.00152	.0010	.00147
.0078	.00150		

TABLE III

DATA OF VAN'T HOFF AND REICHER

$c_{\mathrm{ClCH_2COOH}}$	K_c
0.05	0.00165
.0049	.00151
.00245	.00162
.0003	.00162

$$\alpha = \mu/\mu_\infty$$

where α is the degree of dissociation and μ and μ_∞ are the equivalent conductances of the solution being measured and of the same electrolyte at infinite dilution, respectively, an exact agreement cannot be expected.

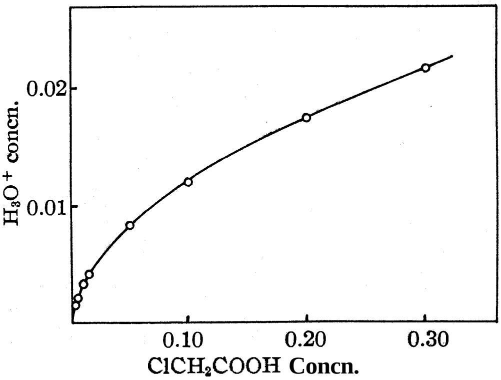

Fig. 1.—The change of H_3O^+ concentration with the concentration of monochloro-acetic acid.

The results given in the first two columns of Table I are plotted in Fig. 1, showing the variation of the H_3O^+ concentration with the acid concentration. In Pig. 2 the log K_c has been plotted against $\sqrt{\mu}$, showing a

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[3] Ostwald, *Z. physik. Chem.*, 3, 170 (1889).

[4] Van't Hoff and Reicher, *ibid.*, 2, 777 (1888).

curve of the form required by Equations 6 and 7. From this curve and the third and fifth columns of Table I, we find the following expression for

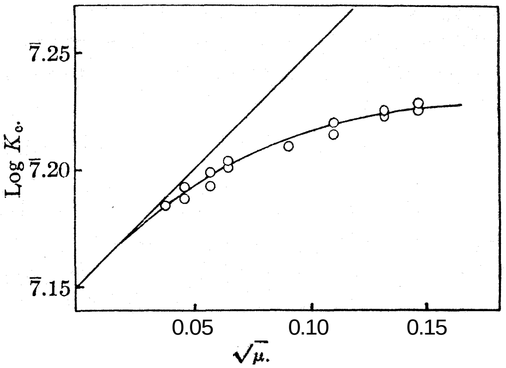

Fig. 2.—The relation of log K_c to $\sqrt{\mu}$.

the dissociation of pure monochloro-acetic acid in the concentration range 0.003 to 0.300 molar

$$\log K_c = (7.150 - 10) + \sqrt{\mu} - 3.2\mu$$

Summary

1. The H_3O^+ concentrations of solutions of monochloro-acetic acid from 0.003 to 0.300 molar have been determined.

2. From these measurements, the dissociation constant of monochloro-acetic acid has been determined. It has been shown to vary with the ionic strength in the manner required by theory.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

A MERCURY–BASIC MERCURIC SULFATE VOLTAIC CELL[1]

BY WARREN C. VOSBURGH AND OSCAR N. LACKEY

RECEIVED DECEMBER 3, 1929 PUBLISHED APRIL 7, 1930

The lead storage cell can be considered as a modification of the cell

$$M \mid M^{I}X \text{ (sat.)} \mid MIX \text{ (sat.)}, M^{II}X_2 \text{ (sat.)} \mid \text{(Pt)} \qquad (1)$$

where M' and M^{II} stand for a metallic element in two states of oxidation and $M^{I}X_2$ has a small solubility. In the storage cell $M^{I}X$ is lead sulfate, but $M^{II}X_2$ is replaced by the higher oxide. Sulfuric acid must then be present in the electrolyte, and the electromotive force depends upon the concentration of the acid.

It has been found in this investigation that a cell analogous to the lead storage cell, namely

$$\text{Hg} \mid Hg_2SO_4,\ xM\ H_2SO_4 \mid xM\ H_2SO_4,\ Hg_2SO_4,\ 3HgO{\cdot}SO_3 \mid \text{(Au)} \qquad (2)$$

is reproducible and constant over short periods of time.

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[1] Taken from a thesis presented by Oscar N. Lackey in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Duke University in June, 1929.

Preparation of Materials

Mercurous sulfate was prepared by precipitation from recrystallized mercurous nitrate and C. P. sulfuric acid solution.

Basic mercuric sulfate was prepared by slowly adding mercuric oxide to 5 *M* sulfuric acid, diluting with ten times its volume of water, and boiling until no more yellow precipitate was obtained. According to Hoitsema[2] the substance obtained under such conditions is the yellow compound $3HgO \cdot SO_3$.

Mercury was purified by washing with mercurous nitrate solution and distilling under reduced pressure in a current of air.

Sulfuric acid solutions were prepared from C. P. acid and were standardized by titration with standard sodium hydroxide solution.

Experimental

Preparation of the Cells.—The cells were set up in vessels of the type used by Vosburgh and Craig,[3] an H-shaped vessel with a side-arm for the introduction of materials. The mercurous sulfate electrode was set up in the plain leg of the vessel. In the other leg a gold-plated platinum wire[4] was fixed in place and enough of a mixture of mercurous sulfate, basic mercuric sulfate and the sulfuric acid electrolyte was poured in to completely cover the wire. The vessel was then filled to a point above the cross-arm with the sulfuric acid solution. No precautions were taken to protect from air.[5]

Electromotive Force Measurements.—The cells were immersed in an oil thermostat at 25 ± 0.02° and electromotive force measurements were made daily until constancy over a period of several days was assured. The final values differed from the values obtained at the end of the first day less than 1 mv. Constancy within two or three hundredths of a millivolt was obtained within from three to seven days and the cells were observed for from four to seven days longer. All cells had been made in duplicate (triplicate in the case of the 0.0954 M electrolyte) and duplicates agreed within 0.2 mv., except in the case of the cells with the most dilute electrolytes, in which case it was within 0.3 mv. When constancy at 25° was attained, the temperature of the thermostat was changed successively to 20, 30, 35, 30 and 25° and measurements were made at each temperature, after allowing thirty to thirty-six hours for the attainment of constancy.

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[2] Hoitsema, *Z. physik. Chem.*, 17, 656 (1895).

[3] Vosburgh and Craig, THIS JOURNAL, 51, 2012 (1929).

[4] No. 28 platinum wire was sealed into a glass tube with about 4 cm. projecting. The wire was wound in the form of a helix and gold-plated. Preliminary experiments had shown that gold-plated electrodes gave greater sensitivity than plain platinum electrodes. Platinized platinum electrodes gave somewhat erratic results when the cells were first set up.

[5] See Randall and Stone, THIS JOURNAL 51, 1752 (1929).

The results are given in Table I, the successive columns of electromotive force values being given in the order in which the measurements were made.

TABLE I

ELECTROMOTIVE FORCES AT VARIOUS TEMPERATURES

H_2SO_4 M/l.	Electromotive force, v. 25°	20°	30°	35°	30°	25°	$\Delta E/AT$ v./degree
0.1450	0.2113	0.2129	0.2098	0.2082	0.2097	0.2113	−0.00031
.0954	.1975	.1992	.1957	.1940	.1957	.1974	− .00034
.04724	.1744	.1764	.1724	.1704	.1724	.1744	− .00040
.02385	.1505	.1527	.1482	.1460	.1482	.1504	− .00044
.01194	,1258	.1281	.1234	.1211	.1234	.1257	− .00046

Comparison of the first and second sets of measurements at 25 and at 30° indicates that no change in electromotive force other than that caused by the temperature took place. The electromotive force is a linear function of the temperature within the limits of error.

Over a period of about six months, the cells showed a decrease in electromotive force of from 0.7 to 15.5 mv. The cells with the more dilute electrolytes decreased considerably less than those with the more concentrated electrolytes. A decrease is to be expected because diffusion of mercuric ion to the mercury electrode and its reaction with mercury would involve using up some of the sulfuric acid of the electrolyte.

$$3HgO\cdot SO_3 + 3Hg + 2H_2SO_4 \longrightarrow 3Hg_2SO_4 + 2H_2O$$

Solubility of Basic Mercuric Sulfate.—The rate of diffusion of mercuric ion to the mercury electrode must depend on the solubility of basic mercuric sulfate, which increases with the sulfuric acid concentration. For a concentration of 0.0127 M at 25° Cox[6] found a mercuric oxide concentration of 0.0007 M. Data for concentrations in the vicinity of the more concentrated solutions used in the present work seemed to be lacking, so a few determinations were made. The sulfuric acid solutions were saturated with basic mercuric sulfate at room temperature, 25 to 30°. Mercury was determined in samples by titration with standard thiocyanate solution. The results are given in Table II.

TABLE II

SOLUBILITY OF BASIC MERCURIC SULFATE

H_2SO_4 concn., M/l	Sample, cc.	0.0977 M NH_4CNS, cc.[a]	Concentration, M/l HgO	SO_3
0.1450	100	40.81	0.0203	0.1518
.0954	100	26.31	.0131	.0998
,01194	100	2.07	.00103	.01228

[a] Each value is the average of three closely agreeing results.

The appreciable solubility of the basic mercuric sulfate makes energy data calculated from the results in Table I uncertain.

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[6] Cox, *Z. anorg. Chem.*, 40,146 (1904).

Summary

The cell Hg | Hg_2SO_4, xMH_2SO_4 | xMH_2SO_4, $Hg_2SO_4,3HgO \cdot SO_3$ | (Au) has been set up and its electromotive force measured. It is fairly reproducible, and constant in electromotive force for a short period soon after it is set up, but the e. m. f. decreases slowly over a period of several months.

The solubility of basic mercuric sulfate in some of the sulfuric acid electrolytes was measured.

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

CATALYSIS IN THE HYDRATION OF PROPIONIC ANHYDRIDE[1]

BY MARTIN KILPATRICK, JR.

RECEIVED DECEMBER 3, 1929 PUBLISHED APRIL 7, 1930

In a recent investigation of catalysis in the hydration of acetic anhydride[2] it was shown that while bases other than hydroxyl ion exert a catalytic effect, the magnitude of the effect is not in the order of increasing basic strength of the catalyst as it is in other cases.[3] Thus it was found that the formate ion accelerates the reaction to a marked degree, the acetate ion to a lesser extent, while in the presence of propionate ion the reaction is slower than in water alone. From the theory the reverse order was to be expected. The possibility of mixed anhydride formation was offered in explanation of the experimental results.

The question may be raised as to whether the hydration of acetic anhydride is an exception to the general theory, or a chemical process which may not be classed as a catalytic reaction at all. It remains, however, that a study of the facts is far more useful than debating the catalytic or non-catalytic nature of the reaction.[4]

The experimental results obtained in the case of acetic anhydride suggest that when the reaction is retarded there is partial formation of the mixed anhydride, or some other intermediate compound formed from the anhydride and the ion in question, which has the same order of stability as the mixed anhydride. It is therefore desirable to know the relationships which exist in the hydration of propionic and acetopropionic anhydrides. The present paper deals with the effect on the hydration of propionic

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[1] Paper presented at the Minneapolis Meeting of the American Chemical Society, September, 1929.

[2] Kilpatrick, THIS JOURNAL, 50, 2891 (1928).

[3] Bronsted and Pedersen, *Z. physik. Chem.*, *113*, 389 (1924); Bronsted and Guggenheim, THIS JOURNAL, 49, 2554 (1927); Bronsted, *Trans. Faraday Soc.*, *24*, 630 (1928).

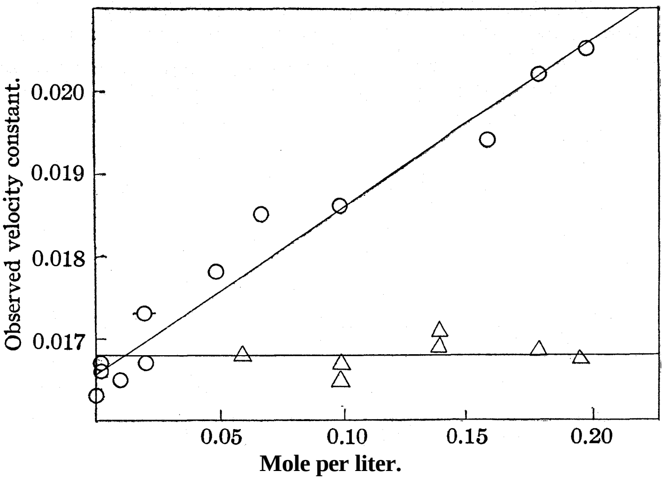
[4] In this connection see Hinshelwood, *ibid.*, 24, 552 (1928).

anhydride of hydrogen, formate, acetate and propionate ions; it also includes a study of the "solute effect"[5] upon the reaction.

Experimental Part

The apparatus, the experimental procedure and the method of calculation were the same as those described in the previous paper. As before, all experiments were carried out at 0°.[2]

Propionic anhydride was obtained from three different sources. The first sample distilled at 164–165° under 769 mm.; it gave the same rate of hydration as the second, which under 16 mm. distilled at 62.5–63.3°. In fact both samples gave, within the experimental reproducibility of the measurements (2%), the same rate as the third sample, c. p. propionic anhydride.



○, HCl; △, NaCl; -⊙-, 0.02 HCl + 0.06 NaCl.

Fig. 1.—affect of H_3O^+ on reaction rate. Effect of NaCl.

The velocity constant of the spontaneous reaction was measured in solutions 0.002 M in hydrochloric acid; here any catalytic effects of the hydrogen, hydroxyl and acetate ions are negligible. The velocity constant, k_0, was found to be 0.0166 min.$^{-1}$; the value given by Verkade[6] is 0.0161. The half time of the reaction is forty-three minutes as compared with twenty-six minutes in the case of acetic anhydride.

The effect upon k_0 of the addition of sodium chloride is shown by the data recorded in Table I, and again, graphically, by the lower line of Fig. 1. In all cases the solutions were 0.002 M in hydrochloric acid and 0.046 M in propionic anhydride.

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[5] This term has been proposed by Walker to designate the effect of non-electrolytes as well as of electrolytes (other than catalysts) upon the reaction. Walker, *Trans. Faraday Soc.*, 24, 722 (1928).

[6] Verkade, Rec. *trav.* chim., 35, 79 (1915).

TABLE I

EFFECT OF SODIUM CHLORIDE

All solutions 0.002 M in HCl. Temperature, 0°

NaCl, moles per liter	0.0	0.059	0.099	0.139	0.179	0.195	0.743
k, observed	.0166	.0168	.0165 .0167	.0171 .0169	.01685	.01675	.0133

There is possibly an increase in rate in dilute solution with addition of sodium chloride; its magnitude, however, does not exceed the experimental error of the measurements.

Table II shows the effect of the hydrogen ion upon the rate of hydration. In the second column are recorded the observed velocity constants, in the third, the differences between $k_{\text{obs.}}$ and k_0, k_0 being taken as 0.0166 on the assumption that the salt effect upon the spontaneous reaction is negligible. The constant of hydrogen ion catalysis, $k_{\text{H}_3\text{O}^+}$, is obtained by dividing $k_{\text{obs.}} - k_0$ by the concentration of hydrochloric acid.

TABLE II

EFFECT OF HYDROGEN ION

HCl, moles per liter	k, observed	$k_{\text{obs.}} - k_0$	$k_{\text{H}_3\text{O}^+}$
0.0020	0.0166	....	...
.0100	.0165	....	...
.0200	.0167	....	...
.0485	.0178	0.0012	0.025
.0667	.0185	.0019	.028
.0990	.0186	.0020	.020
.1590	.0194	.0028	.018
.1790	.0202	.0036	.020
.1980	.0205	.0039	.020
.743	.0334	.0201	.027[a]
		Average,	.022 a. d. 15%

[a] Omitted from average; k_0 here 0.0133.

In taking the average value of $k_{\text{H}_3\text{O}^+}$, the last experiment in the table was omitted, for at a concentration of 0.7 M one cannot assume that the salt effects of hydrochloric acid and of sodium chloride are the same. In fact, there is some doubt of the justifiability of this assumption in dilute solution. In the case of acetylchloro-aminobenzene, Soper and Pryde[7] have shown that the effects may even be in opposite directions. It is also possible that a salt effect upon the hydrogen ion catalyzed reaction is coming into evidence at this high concentration.

The reaction is retarded by acetic acid and by propionic acid, as is shown in Table III and Fig. 2.

For acid concentrations up to 1 M, the effect of acetic acid upon k_0 may

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[7] Soper and Pryde, *J. Chem. Soc.*, 2761 (1927).

TABLE III

EFFECTS OF ACETIC AND PROPIONIC ACIDS

Init. concn. of acetic acid, moles per liter	$k_{obs.}$		Init. concn. propionic acid, moles per liter	$k_{obs.}$	
0.194	0.0155				
.388	.0156		0.394	0.0150	
.582	.0148,	0.0151	.594	.0144	
.799	.0144		.795	.0136	0.0136
.970	.0139		.990	.0128	0.0127
1.940	.0118		1.970	.0101	

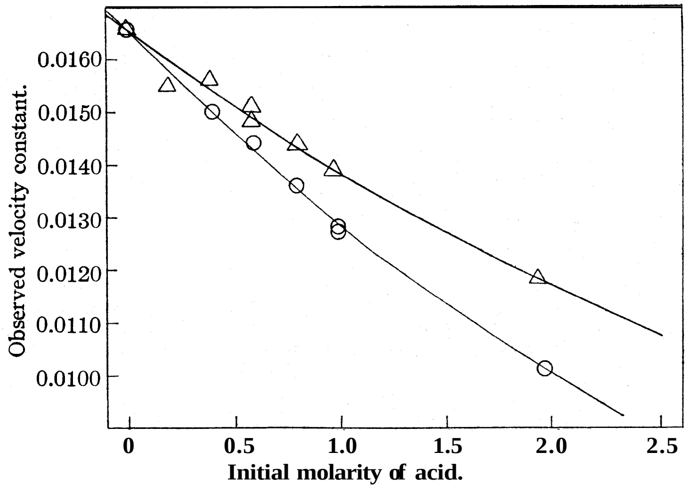
be expressed, with an accuracy greater than the experimental reproducibility, by the equation

$$k_{obs.} = 0.0166 - 0.0028\,m$$

and the effect of propionic acid by the equation

$$k_{obs.} = 0.0166 - 0.0039\,m$$

The effects are accordingly spoken of as "linear."



△, Acetic; ○, propionic.

Fig. 2.—Effect of acetic acid. Effect of propionic acid.

This term is in itself somewhat incomplete. The rate of the reaction between two non-electrolytes A and B is given, according to Bronsted, by the equation

$$v = k(A)(B)f_A f_B/f_{AB} \tag{1}$$

where k, the velocity constant, is constant for a given reaction, temperature and medium. When the reaction is carried out in the presence of the non-electrolyte or the weak electrolyte C, a change in the rate, accompanying the change in medium, may be expected. This change in rate may result from change in the velocity constant k, or from changes in the activity coefficients f_A, f_B and f_{AB}. From the rather scanty evidence existing[S] it appears justifiable to assume that

$$\ln f_A = \beta_A m \tag{2}$$

where β_A is a constant for the substance A dissolved in an aqueous solution of C, and m is the concentration of C present. If we for the moment assume that k remains unchanged in the presence of C and that change in rate arises only from changes in the activity coefficients

$$k_{obs.} = k f_A f_B / f_{AB} \tag{3}$$

Substituting the values of the activity coefficients from Equation *2* in *3,* we have

$$k_{obs.} = k e^{m(\beta_A + \beta_B - \beta_{AB})}$$

or

$$k_{obs.} = k e^{m\sigma}, \text{ where } \sigma = \beta_A + \beta_B - \beta_{AB} \tag{4}$$

When $e^{m''}$ is expanded into a series, (4) becomes

$$k_{obs.} = k(1 + (\sigma m)/1! + (\sigma m)^2/2! + (urn)^3/3! + \dots.) \tag{5}$$

The initial slope of the curve obtained by plotting $k_{obs.}$ against m determines **a.** 'She same type of equation is applicable in the case of a reaction between a non-electrolyte and an ion in dilute electrolyte solution.[9]

In order to apply Equation 5 to the results given in Table III, it is necessary to calculate the velocity constants per liter of solution in terms of equal weights of water, water being a reactant, and to make a small correction for catalysis by hydrogen and acetate or propionate ions. In Table IIIA are recorded the observed values of the velocity constant per liter of solution per 1000 g. of water, and the values of this constant calculated by Equation *5.*

TABLE IIIA

MEDIUM EFFECTS OP ACETIC AND PROPIONIC ACIDS

CH_3COOH, moles per liter	k/liter/ 1000 g. H_2O, obs.	k/liter/ 1000 g. H_2O, calcd.	C_2H_5COOH, moles per liter	k/liter/ 1000 g. H_2O, obs.	k/liter/ 1000 g. H_2O, calcd.
0.194	0.0156	0.0162			
.388	.0158	.0157	0.394	0.0154	0.0154
.582	.01525	.01535	.594	.0150	.0149
.799	.01485	.0149	.795	.0143	.01435
.970	.0144	.0146	.990	.01355	.01385
1.940	.0128	.0128	1.970	.01145	.0116
	$\sigma = -0.134$			$\sigma = -0.182$	

It should therefore be borne in mind that the statement that the effect of change in the nature of the medium upon the velocity constant is a linear effect does not mean that the relationship between the velocity constant and the concentration of added solute is exactly

$$k = k_0 + \sigma m$$

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[8] Randall and Failey, *Chemical Reviews,* 4, *271 (1927).* See also Scatchard, THIS JOURNAL, 52, *52 (1930).*

[9] Bronsted, "Om Syre-og Basekatalyse," Festskrift, Københavns Universitet. *1926,* p. *51.*

It means, rather, that for a given range of concentration the relationship above expresses the experimental results with sufficient accuracy. While k in Equation 1 remains constant, the magnitude of a obviously determines the extent of the valid range.

Table IV gives the results of the experiments carried out in sodium propionate–propionic acid buffer solutions.

TABLE IV

EFFECT OF PROPIONATE

C_2H_5COONa, moles per liter	C_2H_5COOH, moles per liter	$k_{obs.}$	k_0'	$k_{obs.} - k_0'$	k_{P^-}
0.0497	0.940	0.0139	0.01305	0.00085	0.017
.0994	.885	.0151	.01325	.00185	.018
.1490	.835	.0155	.0134	.0021	.014
.1990	.785	.0162	.0136	.0026	.013
.1980	.394	.0170	.0147	.0023	.012
.247	.736	.0172	.01375	.00345	.014

Average, 0.015 a. d., 13%

Here k_0' (Col. 4) is k_0 corrected for the effect of the propionic acid; the effect of the electrolyte upon the medium is assumed to be negligible, as was found in the case of sodium chloride. The constant of propionate ion catalysis (Col. 6) is obtained by dividing $k_{obs.} - k_0'$ by the propionate ion concentration, which may be taken equal to the concentration of the sodium salt.

In an entirely similar way Table V records the results of the experiments in sodium acetate–acetic acid buffer solutions.

TABLE V

EFFECT OF ACETATE

CH_3COONa, moles per liter	CH_3COOH, moles per liter	$k_{obs.}$	k_0'	$k_{obs.} - k_0'$	k_{AC^-}
0.0497	0.920	0.0157	0.01405	0.00165	0.035
.0994	.881	.0174	.01415	.00325	.033
.1490	.831	.0194	.01425	.00515	.0345
.1990	.771	.0210	.0144	.0066	.033
.1980	.933	.0212	.0140	.0072	.036

Average. 0.034 a. d., 3%

The catalytic effect of the acetate ion is more than twice that of the propionate ion. Tables II, IV and V show the parallelism between the magnitude of the catalytic constant and the average deviation of its experimental values from the mean. It may be mentioned that, for the lowest concentration of catalyst employed, an error of 1% in $k_{obs.}$ causes an error of 15% in $k_{H_3O^+}$, an error of 17% in $k_{propionate}$, and an error of 10% in $k_{acetate}$.

The results of the experiments in sodium formate–formic acid buffer solutions are summarized in Table VI and are represented graphically in Fig. 3.

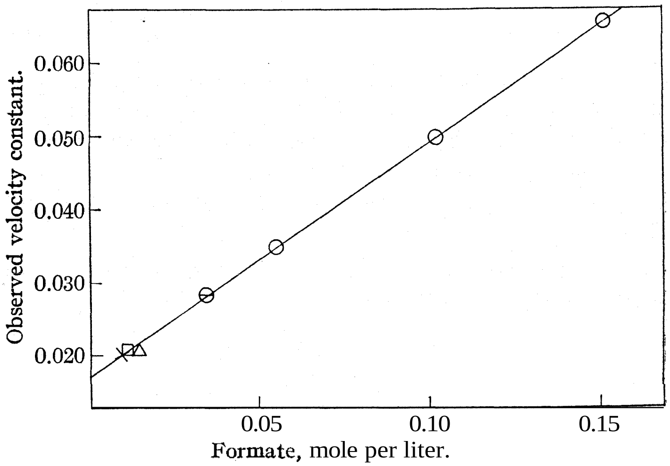
TABLE VI

EFFECT OF FORMATE

HCOOH, moles per liter	HCOONa, moles per liter	H_3O^+, moles per liter	$HCOO^-$, moles per liter	$k_{obs.}$	$k_{obs.} - k'_0$	k_{F^-}
0.397	0	0.0093	0.0093	0.0202	0.0033	0.35_5[a]
.593	0	.0114	.0114	.0205	.0036	$.31_5$[a]
.937	0	,0145	.0145	.0206	.0037	.26[a]
.971	.0249	.0096	.0345	.0281	.0112	.325
.994	.0497	.0051	.0548	.0347	.0178	.325
.994	.0992	.0031	.1023	.0496	.0327	.319
.994	.1491	.0023	.1514	.0652	.0483	.319
					Average,	0.322, a. d. 1%

[a] Not included in average.

In calculating the hydrogen- and formate-ion concentrations, values of the dissociation constant of formic acid were obtained from the empirical equation given by Brönsted[10] for solutions less than 0.05 M in sodium formate, while for the more concentrated salt solutions preliminary values[11] determined in this Laboratory were used.



Formic acid: ×, 0.397; O, 0.593; A, 0.937; ⊖, 0.971; ⊙, 0.994 mole per liter.

Fig. 3.—Effect of formate.

For several reasons it is hardly feasible to determine the medium effect of formic acid upon the rate of hydration by carrying out a series of experiments in solutions of constant formate and varying formic acid concentration. In the first place, the concentration of formic acid must be kept high enough to prevent a shift in the buffer equilibrium. In the second

[10] Bronsted and Volquartz, *Z. physik. Chem.*, *134*, 100 (1928).

[11] The dissociation constant was measured catalytically by the method employed by Bronsted and Wynne-Jones, *Trans. Faraday Soc.*, *25*, 59 (1929).

place, the catalytic effect of the formate ion is so large compared to the effect sought that the latter would be concealed by a slight change in the formate-ion concentration. The intercept on the axis of velocity constants (Fig. 3) has therefore been taken to represent the velocity constant of the spontaneous reaction in a solution 1 M in formic acid. The intercept is 0.0169, a value which may be in error due to a salt effect upon the formate ion catalyzed reaction. The product $(H_3O^+)k_{H_3O^+}$ varies from 0.00021 to 0.00007 in the second group of experiments listed in Table VI, the experiments from which k_{formate} has been calculated. In view of the smallness of the correction, and the uncertainty of the intercept, the hydrogen-ion catalysis has been neglected. The sixth column of Table VI gives the difference between the observed velocity constant and k'_0, which is k_0 corrected for the effect of the formic acid, or 0.0169.

A few experiments were carried out to determine the effect of the butyrate ion. In a solution 0.995 M in butyric acid, $k_{\text{obs.}}$ was found to be 0.0123; in a solution 0.0497 M in sodium butyrate and 0.995 M in butyric acid, $k_{\text{obs.}}$ was approximately 0.0113. The velocity constant obtained in the presence of butyrate is recorded as "approximate" because the reaction in the butyrate–butyric acid buffer solution was not exactly monomolecular. The effect of butyrate is $(0.0113 - 0.0123)/(0.050)$ or -0.020.

Again, the catalytic effects of the anions studied fail to follow the order of basic strength of the catalyst. With propionic, as with acetic anhydride, the formate ion is a remarkably good catalyst. No catalytic effect of molecular acid upon the reaction has been detected; if it exists, it is masked by the effect of the acid upon the medium. In the present investigation no new fact has come to light which invalidates the idea of mixed anhydride formation suggested in the previous paper. In a following paper there will be presented the results of a study of the hydration of acetopropionic anhydride.

The author wishes to express his gratitude to the Laboratory of Physical Chemistry of the Polytechnic Institute of Copenhagen for the gift of the dilatometer in which these measurements were made. He wishes also to thank the Department of Physiological Chemistry of the University of Pennsylvania for the use of its refrigerator room, which made possible work at 0° during the summer months.

Summary

1. The salt or electrolyte effect of sodium chloride upon k_0, the velocity constant of the spontaneous hydration of propionic anhydride, has been found to be negligibly small, in dilute solution, at 0°.

2. The hydration of propionic anhydride is retarded by acetic acid and by propionic acid. The linear nature of these effects has been discussed.

3. The constants of hydrogen, propionate, acetate and formate ion catalysis have been determined. They are in the order

$$k_{\text{propionate}} < k_{\text{H}_3\text{O}^+} < k_{\text{acetate}} < k_{\text{formate}}$$

4. The hydration of propionic anhydride is retarded by butyric acid. It is further retarded by the butyrate ion.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

CATALYSIS IN THE HYDRATION OF ACETOPROPIONIC ANHYDRIDE[1]

BY MARTIN KILPATRICK, JR., AND MARY L. KILPATRICK

RECEIVED DECEMBER 3, 1929 PUBLISHED APRIL 7, 1930

In two previous papers[2] there have been presented the results of a study of the hydration of acetic and of propionic anhydride. The hydration is catalyzed by the hydrogen ion and the hydroxyl ion, and by bases other than the hydroxyl ion; the catalytic constants of the bases are not, however, in the order of their basic strength. Moreover, the propionate ion retards the hydration of acetic anhydride, and accelerates the hydration of propionic anhydride, while the butyrate ion retards both processes. It was suggested that, where retardation occurs, there is formation of the mixed anhydride, or some other intermediate compound, of the order of stability of the mixed anhydride, formed between the simple anhydride and the anion. In the present paper are given the results of the measurement of the rate of hydration of one of these mixed anhydrides, the acetopropionic, at 0°.

Experimental Part

The apparatus, experimental procedure and the method of calculation have already been described.[2]

The existence of mixed anhydrides has been the subject of much discussion, due, primarily, to their property of slowly decomposing during distillation into the simple anhydrides[3] Because of the lack of a definite boiling point, many chemists regarded the mixed anhydrides as equimolecular mixtures of the corresponding simple anhydrides. With the preparation of certain of the higher mixed anhydrides, which are crystalline solids at ordinary temperatures, the doubt of the existence of this class of compounds disappeared. Verkade[4] succeeded in preparing the liquid aceto-

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[1] Paper presented at the Minneapolis Meeting of the American Chemical Society, September, 1929.

[2] (a) Kilpatrick, THIS JOURNAL, 50, 2891 (1928); (b) Kilpatrick, *ibid.*, 52, 1410 (1930).

[3] Behal, *Ann. chim. phys.*, [7] *19*, 274 (1900).

[4] Verkade, *Rec. trav. chim.*, 35,299 (1915).

propionic anhydride in a state of purity such that it reacted with water in dilute aqueous solution according to the monomolecular law. If Verkade had had a mixture of acetic and propionic anhydrides, he would have obtained a constant only in the event that the two simple anhydrides took up water at the same rate, which is not true.

The acetopropionic anhydride used in the present investigation was prepared by two methods: from propionyl chloride and anhydrous sodium acetate, as described by Verkade,[4] and from acetyl chloride and propionic acid in the presence of pyridine, in ethereal solution.[5] The first three columns of Table I list the samples, their boiling points, and the pressures under which they distilled.[6]

Table I

The Spontaneous Reaction

Temperature, 0°. All solutions 0.0004 M in HCl

Sample	Boiling point, °C.	Pressure, mm.	k_0	Volume change, cc. per liter per 0.05 mole of anhydride
A	53–56	17–19	0.0222, 0.0223	0.145, 0.14
B	57.8–60.5	19	.0220	.14
C	52–55	17	.0225	.14
D	55–58.5	18	0.0221, 0.0225, 0.0227	0.14, 0.14, 0.14
E	57.4–59.4	22	.0223	.125
F	51–51.5	15.5	.0226	.135

Samples A, B, C, D and E were prepared according to Verkade; in the preparation of F the pyridine method was employed. All except F gave a negative test for chloride. A weighed portion of D, the anhydride used in all the subsequent experiments, was dissolved in water and titrated against standard sodium hydroxide solution. The molecular weight was calculated from the titer to be 115.8; the theoretical is 116.1, and the value found by Verkade, 115.6. The presence of 2% of acetic anhydride as impurity in Sample D would cause the difference of 0.3 between the theoretical and the calculated molecular weight; the determination of the molecular weight is, therefore, not a sensitive test of the purity of the mixed anhydride. The fourth column of Table I records the constant of the spontaneous (water) reaction. In the fifth column of the table is shown the decrease in volume accompanying hydration, calculated for a liter of solution initially containing 0.05 mole anhydride.

To test the possibility of the immediate and complete reaction of the simple anhydrides in aqueous solutions to form the mixed anhydride, the rate of hydration of an equimolecular mixture of acetic and propionic anhydrides was measured. The monomolecular "constant" decreased steadily

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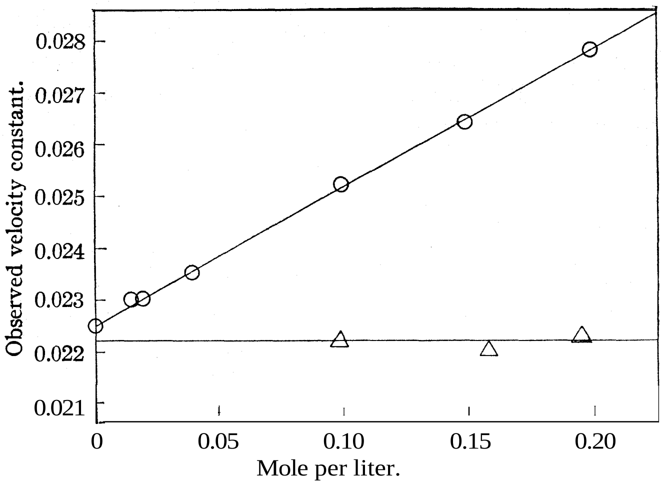
[5] Knoll and Co., German patent 117,267, *Chem. Centr.*, I, 347 (1901); Wedekind, *Ber.*, 35, 2070 (1901).

[6] The authors are indebted to Mr. Clifton Kerns for the preparation of a preliminary sample of acetopropionic anhydride.

with the progress of the reaction. Acetopropionic anhydride is therefore not a mixture.

It will be shown presently that the hydration of acetopropionic anhydride is accelerated by the acetate ion, and retarded by the propionate ion. Both of these ions are present after the start of the reaction, but at concentrations too slight to affect the rate of hydration to a detectable extent.



○, HCl; △, NaCl.

Fig. 1.—Effect of H_3O^+ on reaction rate. Effect of NaCl.

The lower line of Fig. 1 and the data given in Table II show the effect of sodium chloride upon the spontaneous reaction.

Table II

The Effect of Sodium Chloride

Temperature, 0°. All solutions 0.0004 M in HCl

NaCl, moles per liter	0.099	0.158	0.195
k_{observed}	.0222	.0220	.0223

In all the experiments the solutions were 0.0004 *M* in hydrochloric acid and 0.06 M in acetopropionic anhydride, the anhydride concentration being that used throughout the work. If an electrolyte effect exists in dilute solution, it is negligibly small, as in the case of propionic anhydride.

Table III gives the results of the experiments carried out to determine the effect of the hydrogen ion.

In the third column one has the difference between the observed velocity constant and k_0, which is taken as 0.0224 for solutions having equivalent salt concentrations not greater than 0.2. The proportionality between the increase in the velocity constant and the acid concentration is represented by the upper line of Fig. 1.

TABLE III

EFFECT OF HYDROGEN ION

HCl, moles per liter	$k_{\text{obs.}}$	$k_{\text{obs.}} - k_0$	$k_{\text{H}_3\text{O}^+}$
0.0004	0.0224	....	....
.0149	.0230	0.0006	0.040[a]
.0198	.0230	.0006	.030
.0398	.0235	.0011	.028
.0994	.0252	.0028	.028
.1490	.0264	.0040	.027
.1990	.0278	.0054	.027
		Average,	.028 a. d. 3%

[a] Omitted from average.

In Table IV are shown the results of the experiments in sodium acetate–acetic acid buffer solutions. Since it was expected that the medium effect of acetic acid upon k_0 would not differ in character from the medium effect in the hydration of acetic anhydride or propionic anhydride, an investigation of the effect was avoided by using an acid concentration of 0.974 M in all the experiments.

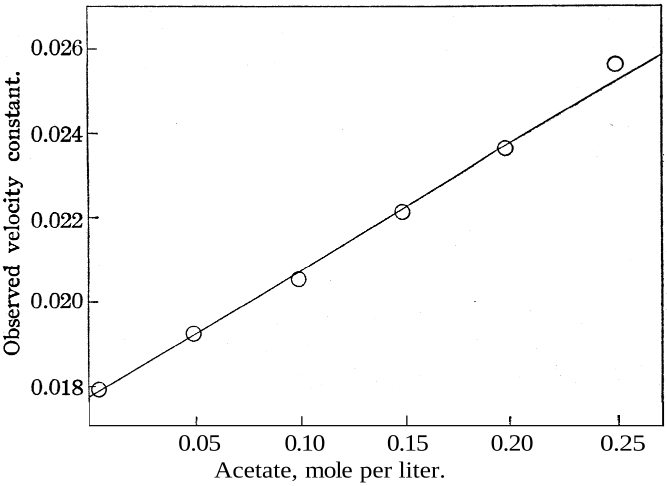


Fig. 2.—Effect of acetate.

In Fig. 2 the observed velocity constants are plotted against the corresponding acetate concentrations; the intercept of the line on the axis of velocity constants gives k_0', the constant of the spontaneous reaction in 0.97 M acetic acid; k_0' is 0.0177.

In the third column of Table IV is recorded the amount of the reaction due to the acetate ion, $k_{\text{obs.}} - k_0'$, and in the fourth, the constant of acetate ion catalysis.

Similar experiments were performed in sodium propionate–propionic acid buffer solutions in which the concentration of propionis acid was kept

TABLE IV

EFFECT OF ACETATE

All solutions 0.974 M in CH_3COOH. $k_0' = 0.0177$

CH_3COO^-, moles per liter	$k_{obs.}$	$k_{obs.} - k_0'$	k_{AC^-}
0.005	0.0179	....	...
.0497	.0192	0.0015	0.030
.0994	.0205	.0028	.028
.1490	.0221	.0044	.029
.1990	.0236	.0059	.030
.2495	.0256	.0079	.032
		Average,	.030 a. d. 3%

0.987 M. The reaction being no longer strictly monomolecular, the velocity constants are recorded as approximate. The deviation from monomolecularity is less with aceto propionic anhydride (not exceeding 5% in any case) than with acetic anhydride, or with propionic anhydride in the presence of butyrate. In Fig. 3 the observed velocity constants are plotted against the propionate concentrations. The constant of the spontaneous reaction in 0.987 M propionic acid, k_0', is 0.0171 as given by the intercept of the line upon the axis of velocity constants.

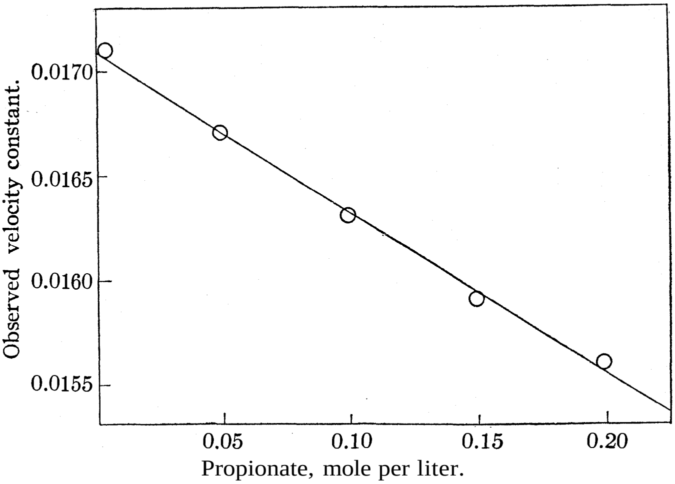


Fig. 3.—Effect of propionate.

TABLE V

EFFECT OF PROPIONATE

All solutions 0.987 M in C_2H_5COOH. $k_0' = 0.0171$

$C_2H_5COO^-$, moles per liter	0.005	0.0497	0.0994	0.1490	0.1990
$k_{obs.}$ (approx.)	.0171	.0167	.0163	.0159	.0156

With increasing propionate concentration the observed velocity constant decreases, and the rate of decrease is proportional to the propionate-ion concentration. In 0.99 M propionic acid solution the constant may be calculated from the equation

$$k = 0.0171 - 0.0077\sim$$

where *c* represents the concentration of propionate. It may be recalled that the propionate ion retards the hydration of acetic anhydride and accelerates the hydration of propionic anhydride.

The butyrate ion, like the propionate, retards the hydration of acetopropionic anhydride. In 0.995 M butyric acid solution the constant of the spontaneous reaction was found to be 0.0166, and in a buffer solution 0.997 M in butyric acid and 0.0498 M in sodium butyrate the observed velocity constant (approximate) was 0.0149. The effect of the butyrate ion is therefore (0.0149 − 0.0166)/(0.0497) or −0.025. Butyrate retards the hydration of all three anhydrides studied—acetic, propionic and acetopropionic.

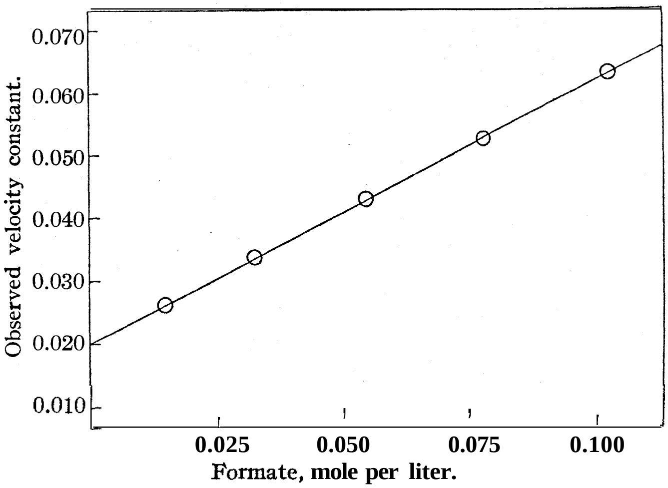


Fig. 4.—Effect of formate.

In Table VI and Fig. 4 are shown the results of the experiments in sodium formate–formic acid buffer solutions. The effect of the 1 M formic

TABLE VI

EFFECT OF FORMATE

HCOOH, moles per liter	HCOONa, moles per liter	H_3O^+, moles per liter	$HCOO^-$, moles per liter	$k_{obs.}$	$k_{obs.} - k'_0$	k_{F^-}
0.992	0	0.0148	0.0148	0.0260	0.0065	0.43[a]
.985	0.0249	.0075	.0324	.03365	.01415	.435
.987	.0497	.0048	.0545	.0431	.0236	.433
.989	.0746	.0035	.0781	.0525	.0330	.423
.990	.0994	.0030	.1024	.0631	.0436	.426

Average, 0.429 a. d. 1%

[a] Omitted from average.

acid upon the spontaneous reaction was again obtained by plotting $k_{\text{obs.}}$ against the formate concentration; the intercept of the line in Fig. 4 upon the axis of velocity constants, 0.0195, represents k_0 or the constant of the spontaneous reaction in 1 M formic acid.

The hydrogen- and formate-ion concentrations were calculated as previously described.[2b] The amount of the reaction due to the hydrogen ion, $(H_3O^+)k_{H_3O^+}$, varies from 0.0004 to 0.0001 in the experiments listed in the table. In view of the smallness of the correction for hydrogen-ion catalysis, and in view of the uncertainty of the intercept (there may exist a small salt effect upon the formate ion catalyzed reaction), no correction for catalysis by the hydrogen ion is made. The sixth column of the table gives the amount of the reaction due to the formate ion, $k_{\text{obs.}} - 0.0195$, and the last column, the constant of formate ion catalysis.

Discussion

The results of the work with the three anhydrides are collected in Table VII.

TABLE VII

SUMMARY OF RESULTS

Anhydride	k_0	$k_{H_2O} = k_0/55.6$	$k_{H_3O^+}$	$k_{CH_3COO^-}$	k_{HCOO^-}	$k_{C_2H_5COO^-}$	$k_{C_3H_7COO^-}$
Acetic	0.0269	0.000484	0.031	0.038_5	0.680	(−0.035)	(−0.049)
Propionic	.0166	.000299	.022	.034	.322	.015	(− .020)
Acetopropionic	.0224	,000403	.028	.030	.429	(− .008)	(− .025)

It will be noticed that the catalytic constants do not stand in the order of basic strength of catalyst, which would require that

$$k_{H_2O} < k_{\text{formate}} < k_{\text{acetate}} < k_{\text{propionate}} < k_{\text{butyrate}}$$

With acetic and with acetopropionic anhydride, the existing order is

$$k_{H_2O} < k_{\text{acetate}} < k_{\text{formate}}$$

while the propionate and the butyrate ion retard the hydration; with propionic anhydride the order is

$$k_{H_2O} < k_{\text{propionate}} < k_{\text{acetate}} < k_{\text{formate}}$$

the butyrate ion again retarding hydration.

An examination of Table VII reveals that with the three anhydrides studied the following statement holds. An anion which has the possibility of reacting with the anhydride to form a different anhydride, and a different anion, accelerates the reaction if the anhydride which might be formed hydrates more rapidly than does the original anhydride, and it retards the reaction when the intermediate anhydride hydrates more slowly than the original. The order in which the anions stand in regard to acceleration or retardation is also the expected order. Thus in the hydration of propionic anhydride

$$k_{\text{acetate}} < k_{\text{formate}}$$

corresponding to the greater reactivity of formic–propionic anhydride than of acetopropionic.

Bronsted's[7] general formula for the velocity of the reaction between A and B has been derived by Bjerrum[8] from the consideration of an equilibrium between the reactants and an intermediate collision complex of which a small fraction reacts in unit time. The concentration of the collision complex S is related to the concentrations of A and B through the equation

$$K = (\mathrm{S})f_\mathrm{S}/(\mathrm{A})(\mathrm{B})f_\mathrm{A}f_\mathrm{B}$$

Since the rate-determining process is the reaction of the complex (either spontaneously or with the solvent) to form the products

$$v = k(\mathrm{S})$$

where k is small, *i. e.*, only exceptionally do A and B collide with sufficient energy to react. Substituting for the concentration of S its value from the equation above, Bjerrum obtained

$$v = kK(\mathrm{A})(\mathrm{B})f_\mathrm{A}f_\mathrm{B}/f_\mathrm{S}$$

Provided the concentration of S is small, so that it is not necessary to distinguish between the concentration of free A or B and its total, measured concentration, and provided the solution is so dilute that the activity coefficient of the complex S may be set equal to the activity coefficient of an ion whose charge equals the algebraic sum of the charges of A and B, the formula is identical with Bronsted's.

The hydration of acetic anhydride may therefore be thought of as proceeding, in water alone, through the formation of the complex $A{\cdot}H_2O$(A representing the anhydride) which then reacts, alone or with water molecules, to give two molecules of acetic acid. The presence of catalysts opens other paths. Thus in the solution of a strong acid

$$A + H_2O \rightleftharpoons A{\cdot}H_2O \qquad (1)$$

$$A{\cdot}H_2O + H_2O \longrightarrow 2CH_3COOH + H_2O$$

$$A + H_3O^+ \rightleftharpoons A{\cdot}H_3O^+ \qquad (2)$$

$$A{\cdot}H_3O^+ + H_2O \longrightarrow 2CH_3COOH + H_3O^+$$

$$-\mathrm{d}A/\mathrm{d}t = k_0(\mathrm{A}) + k_{\mathrm{H_3O^+}}(\mathrm{A})(\mathrm{H_3O^+})$$

In a sodium formate–formic acid buffer solution the reaction also proceeds via the formation of $A{\cdot}HCOO^-$; in a sodium acetate–acetic acid buffer solution, via the formation of $A{\cdot}CH_3COO^-$.

Whenever the formation of a complex of the type $A{\cdot}HCOO^-$ occurs, its reactivity appears to be of the order of magnitude of the reactivity of the mixed anhydride. Table VII shows that the hydration of acetic anhydride is greatly accelerated by the formate ion; this is in accord with the known instability of anhydrides of formic acid. The hydration of propionic anhydride is accelerated by the acetate ion and by the formate ion, the latter

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[7] Brocsted, *Z. physik. Chem.*, 102, *169 (1922).*

[8] Bjerrum, *ibid.*, 108, *82 (1924).*

effect being greater, which is to be expected from the greater instability of formic–propionic anhydride as compared with acetopropionic.

The rate-determining complex formed in the catalyzed reaction cannot, however, be the mixed anhydride itself. If the original anhydride and the catalyzing anion of the buffer reacted to form the mixed anhydride, we should have, for acetic anhydride, say, in a formate–formic acid buffer solution

$$A + \mathrm{HCOO}^- \rightleftharpoons AF + \mathrm{CH_3COO}^-$$

$$K = (\mathrm{AF})(\mathrm{CH_3COO}^-)f_{\mathrm{AF}}f_{\mathrm{CH_3COO}^-}/(\mathrm{A})(\mathrm{HCOO}^-)f_{\mathrm{A}}f_{\mathrm{HCOO}^-}$$

where A represents acetic anhydride, AF, formic–acetic anhydride. The expression for the velocity of reaction becomes

$$v = k(\mathrm{AF})$$

$$v = kK(\mathrm{A})(\mathrm{HCOO}^-)f_{\mathrm{A}}f_{\mathrm{HCOO}^-}/(\mathrm{CH_3COO}^-)f_{\mathrm{AF}}f_{\mathrm{CH_3COO}^-}$$

Since the concentration of the acetate ion changes during the reaction, the mechanism above is not in agreement with the observed monomolecularity of the reaction.

The experimental method employed does not permit wide variation in the initial concentration of anhydride. However, in the study of the hydration of propionic anhydride, in acetate–acetic acid buffer solution, the initial anhydride concentration was changed by 25% without detectable effect upon the velocity constant.

In sodium butyrate–butyric acid buffer solution the hydration of all three anhydrides is retarded; in sodium propionate–propionic acid buffer solution the hydration of acetic and of acetopropionic anhydride is retarded. In these cases there must be immediate chemical reaction to a considerable extent between the anhydride and a constituent of the buffer. Several possibilities present themselves. If the initial anhydride reacted with the anion of the buffer to form another anhydride, and another anion, the rate measured would be the rate of hydration of a mixture of anhydrides, which would not give a monomolecular velocity constant. With increasing concentration of the anion of the buffer the concentration of the intermediate, less reactive, anhydride would increase, making hydration slower. If the anhydride combined with the anion of the buffer to form an addition compound[9] which was itself non-reactive, the rate of hydration would follow the monomolecular law and would decrease with increasing concentration of the anion. The results of the formation of such a compound, in equilibrium with the anhydride, would not be distinguishable from a salt effect. In addition, both processes might go on simultaneously. With acetic anhydride and with acetopropionic anhydride in the presence of propionate or butyrate, and with propionic anhydride in the presence of butyrate, the deviation of the rate of hydration from monomolecularity indicates that there is intermediate anhydride formation.

[9] Franzen, *Ber.*, 41,3641 (1908); Tsakalotos, *Bull. soc. chim.*, [4] 7, 461 (1910).

Summary

1. The salt effect of sodium chloride, in concentrations up to 0.2 M, upon the rate of hydration of acetopropionic anhydride is negligibly small at 0°.

2. The constants of hydrogen, acetate and formate-ion catalysis have been determined. They are in the order

$$k_{H_3O^+} < k_{CH_3COO^-} < k_{HCOO^-}$$

3. The hydration is retarded by the propionate ion and by the butyrate ion.

4. The results obtained with acetic, propionic and acetopropionic anhydrides have been collected. An examination of the catalytic constants suggests that, when the reaction is accelerated in a buffer solution, the collision complex formed between the anhydride and the anion of the buffer is of the order of stability of the mixed anhydride. In those buffer solutions in which the hydration is retarded there is reason to believe that a part of the initial anhydride has reacted with the anion of the buffer to form another anhydride.

PHILADELPHIA, PENNSYLVANIA

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

THE AUTOCATALYTIC REDUCTION OF BROMATE BY HYDROGEN PEROXIDE IN ACID SOLUTION

BY WILLIAM C. BRAY AND PAUL R. DAVIS

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The autocatalytic reduction of bromate ion by hydrogen peroxide has been described briefly by Bray and Livingston.[1] At the acid concentration they used, over 0.7 N, some bromine is formed; its concentration, when hydrogen peroxide is present in excess, rises to a maximum and then gradually decreases to a constant value. We have found that the amount of bromine formed decreases rapidly as the concentration of acid is lowered, and that at moderate or low concentrations of acid (and bromide) the main reaction is

$$BrO_3^- + 3H_2O_2 = Br^- + 3O_2 + 3H_2O \qquad (1)$$

The present investigation was undertaken to measure the rate of this autocatalytic reaction, and to test quantitatively the conclusion[1] that the autocatalysis is due to the reaction

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O \qquad (2)$$

followed by

$$Br_2 + H_2O_2 = O_2 + 2Br^- + 2H^+ \qquad (3)$$

The progress of the reaction was followed by collecting the oxygen over water and measuring its volume. The temperature of the oxygen buret

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[1] Bray and *Livingston,* THIS JOURNAL, 45, 1254 (1923).

and the barometric pressure were noted. The reaction mixture, 250 cc. in volume, was contained in a 500-cc. round-bottomed flask with a long neck, and was shaken vigorously enough to prevent supersaturation. The volume of the evolved oxygen was read frequently and the readings were plotted against the time in minutes. The type of curve obtained is shown in Fig. 1.

The experiments were performed in the dark in a thermostat at 25°. Measured quantities of water and solutions of sulfuric acid, potassium bromate and hydrogen peroxide, all at 25°, were placed in the reaction flask in the order named.

The stock solutions were standardized as follows. The reference for acids and bases was sodium carbonate, and that for potassium permanganate was sodium oxalate. Hydrogen peroxide (diluted "Perhydrol") was titrated with permanganate. Sodium thiosulfate was standardized iodimetrically by means of the permanganate solution.[2] Potassium bromate was determined iodimetrically against thiosulfate.

To test the stoichiometric relations expressed in Equation 1, complete analyses were made in three experiments while some bromate was still present. In one portion of the solution bromide was determined gravimetrically as silver bromide. The bromide concentration thus found was subtracted from the initial bromate concentration to find the bromate concentration in the sample. To another portion of the solution a measured amount of permanganate was added (to destroy the peroxide), and the small excess of permanganate together with the bromate was determined iodimetrically with thiosulfate.[3] From this result and the concentration of bromate as determined above, the concentration of hydrogen peroxide was calculated. While these data proved that the relation between the oxygen formed and the bromate and peroxide used up was almost exactly

$$3 \text{ moles of } O_2 = 1 \text{ mole of } BrO_3^- = 3 \text{ moles of } H_2O_2 \qquad (4)$$

there were slight deviations which indicated that the side reaction

$$2H_2O_2 = 2H_2O + O_2 \qquad (5)$$

could not be completely neglected. Further work showed that this reaction alone took place after the bromate had been completely reduced.

The initial concentrations in moles per liter are shown in Table I in the second to fourth columns. The two experiments of a pair, labeled A and B, were performed simultaneously under identical conditions, except that the concentration of one substance was varied.

The first step toward the interpretation of the results was made by drawing tangents to the oxygen–time curves as close to the origin as possible. The readings in the first five minutes were usually somewhat irregu-

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[2] Bray and Miller, THIS JOURNAL, 45, 2204 (1924).

[3] Cf. Ref. 1, p. 1257.

lar and could be given little weight. The initial rates, cc. of oxygen per min. from 250 cc., are shown in the fifth column of Table I. On account of the initial discrepancies no claim for absolute accuracy can be made, but it is believed that the ratio of the rates in each pair of experiments shows definitely the effect of varying the concentration of one substance. Thus in Expts. 2A and 2B the results in Col. 5 (or 6) show that the rate is doubled when the concentration of hydrogen peroxide is doubled, and therefore that the reaction is first order with respect to the peroxide. The other pairs of experiments furnish evidence that the reaction is also first order with respect to hydrogen ion and bromate ion. The corresponding rate law is

$$-d(BrO_3^-)/dt = (1/3)d(O_2)/dt = k_1(BrO_3^-)(H_2O_2)(H^+) \qquad (6)$$

The values of k_1 in the last column of the Table were calculated by means of Equation 6 by dividing the initial rate, expressed in the unit moles per liter per minute (sixth column), by the product of the initial concentrations. Although these values are not accurate, it seemed justifiable to conclude that $k_1 = 0.04 \pm 0.01$.

Table I

Initial Concentrations and Initial Rates

Expt.	Concentrations, moles/liter (H⁺)	(BrO_3^-)	(H_2O_2)	Cc. O_2 per min. from 250 cc.	$-d(BrO_3^-)/dt \times 10^7$	$k_1 \times 10^3$
1A	0.1	0.00587	0.036	0.017	9	43
1B	.1	.01174	.036	.036	19	45
2A	.12	.00978	.0385	.037	20	44
2B	.12	.00978	.077	.074	40	44
3A	.12	.00489	.0363	.017	9	43
3B	.24	.00489	.0363	.033	18	41
4A	.24	.00493	.0362	.034	18	42
4B	.36	.00493	.0362	.052	28	43

The calculation of the amounts of oxygen formed by the bromide catalysis, Reaction 5, was then undertaken. The method involves the calculation of the rate of this reaction at a series of times in each experiment, the plotting of these rates against the time and the graphic integration from zero time to any designated time. The results of these calculations are shown in the lower half of Table II: x is the concentration of bromide in moles per liter, and the amount of oxygen due to the catalysis is expressed as percentage of the total amount formed. It is to be noted that the oxygen due to catalysis exceeds 0.3% only near the end of Expts. 2B and 3A.

The rates upon which these calculations were based were calculated by means of the differential equation

$$-d(H_2O_2)/dt = {}^1/_2 d(O_2)/dt = k_3(H_2O_2)(Br^-)(H^+) \qquad (7)$$

which has been established by Bray and Livingston.[4] The values of k_3,

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[4] (a) Ref. 1, This Journal, 45, 1258–1271 (1923); (b) Livingston and Bray. *ibid.*, 45, 2048 (1923); (c) Livingston, *ibid.*, 48, 45 (1926); (d) *ibid.*, 48, 53 (1926); (e) Bray and Livingston, *ibid.*, 50, 1654 (1928).

TABLE II

PROPORTION OF OXYGEN DUE TO BROMIDE CATALYSIS

Expt.	1A	1B	2A	2B	3A	3B	4A	4B
Ionic strength, μ	0.156	0.162	0.190	0.190	0.185	0.365	0.365	0.545
ν	.96	.93	.95	.95	.97	.99	.99	.99
γ_{HBr}	.66	.66	.65	.65	.65	.60	.60	.58
10^3k_3	22	22	20	20	20	17	17	16
PERCENTAGE OF OXYGEN DUE TO BROMIDE CATALYSIS								
$10^4 x$								
10	0.21	0.10	0.10	0.15	0.20	0.09	0.11	0.07
20	.23	.11	.10	.19	.23	.12	.12	.09
40			.11	.23	.57	.18	.18	.13
80			.13	.33				
90			.15	.60				

given in Table II, are based on the early experimental data in sulfuric acid solution.[4a] They exceed by only 5 to 15% the values calculated later[4d] by means of the relation $k_3 = 0.043\gamma^2$, where γ is the activity coefficient of hydrobromic acid in the presence of excess sulfuric acid.[4c] The ionic strength of each solution, μ, the proportion of the ionic strength due to the sulfuric acid, ν, and the corresponding values of γ_{HBr} are shown in the table.

Equation 7 was used in the form

$$-d(H_2O_2)/dt = {}^1/_2d(O_2)/dt = k_3(D-3x)(x)(H^+) \qquad (8)$$

Values of $D - 3x$ and x at various times were determined from the amounts of total evolved oxygen on the assumption that Equations 1 and **4** are correct. The amounts of oxygen formed catalytically (calculated as explained above) turned out to be so small that it was unnecessary to repeat the calculation to obtain more exact values.

TABLE III

EXPERIMENTAL DATA CORRECTED FOR BROMIDE CATALYSIS

	1A		1B		2A		2B	
	Times, min.		Times		Times		Times	
$10^4 x$	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.
1	89	113.3	48	61.8	45	59.1	..	33.8
2	155	183.1	92	98.0	87	91.4	44	56.8
3	208	234.2	120	123.9	113	114.0	65	74.4
5	291	308.7	157	160.8	144	145.6	93	100.8
10	426	428.5	214	217.6	193	193.7	139	143.8
15	512	511.1	252	254.4	224	224.8	170	172.7
20	581	578.6	282	282.3	250	248.9	195	195.3
30	696	696.8	326	325.6	287	286.3	231	231.3
40					318	317.6	262	261.5
50					347	346.6	289	289.7
60					376	376.0	318	318.4
70					409	408.5	349	350.2
80					447	449.5	385	390.3
90					512	516.2	441	456.1
95							489	530.8

Table III (Concluded)

	3A		3B		4A		4B	
	Times		Times		Times		Times	
$10^4 x$	Obs.	*Calcd.*	Obs.	*Calcd.*	Obs.	*Calcd.*	Obs.	*Calcd.*
1	120	125.6	63	54.6	41	46.1	20	20.8
2	190	194.1	81	79.1	63	69.5	31.5	32.0
3	238	242.2	99	96.7	80	85.4	39.5	39.9
5	307	310.6	121	120.0	106	107.8	50.5	51.1
10	419	419.0	154	155.8	143	142.7	68.5	68.8
15	494	494.3	177	180.0	167	166.7	81	81.0
20	560	557.4	198	200.8	187	186.7	91	91.3
30	678	676.1	240	239.0	225	224.2	111	110.4
40	828	826.2	290	287.2	271	270.8	135	134.4
45	1000	962.8	337	330.9	308	311.6	156	155.4
47			389	366.3	333	342.4	171	171.2

These results were used to correct the values of x, the bromide concentration. In Table III are shown the corrected values of x and the corresponding "observed" times for all the experiments;[5] in Fig. 1 the same data for Expts. **4A** and 4B are represented by circles. The "calculated" times, also shown in Table III, correspond to the smooth curves in Fig. 1 and will be explained later.

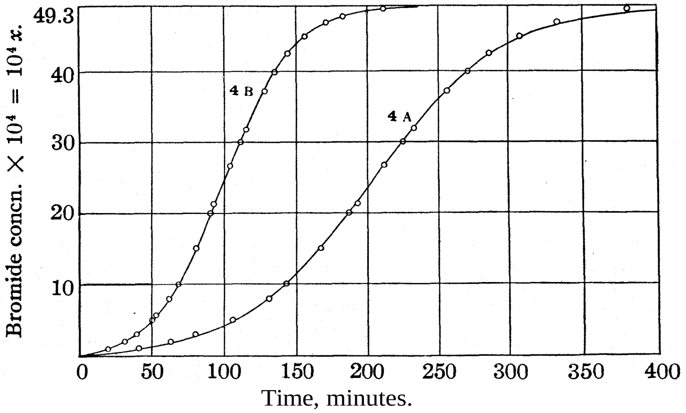

Fig. 1.—Experimental data corrected for bromide catalysis, *cf.* Table III. The smooth curves are calculated from Equation **13** and the constants of Table IV.

The results of Judson and Walker[6] and of Skrabal and Weberitsch[7] leave no doubt that the reduction of bromate by bromide, Equation 2, is represented by the differential equation

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[5] No attempt was made to correct for the discrepancies observed in the first five minutes. If this had been done, the values of $10^4 x$ in the table would have been decreased by about 0.05 in Expts. 1A, 1B and 4A; 0.1 in Expts. 2A and 2B; and **0.15** in Expt. 4B; and might have been slightly increased in Expts. **3A** and 3B.

[6] Judson and Walker, *J. Chem. Soc.,* 73,418 (1898).

[7] Skrabal and Weberitsch, Monatsh., 36,211 (1915).

$$-d(BrO_3^-)/dt = k_2(BrO_3^-)(Br^-)(H^+)^2 \qquad (9)$$

and is rapid enough to account qualitatively for the autocatalysis. Our problem was to determine whether the data of Table III could be accurately represented by the sum of Equations 6 and 9

$$-d(BrO_3^-)/dt = k_1(BrO_3^-)(H_2O_2)(H^+) + k_2(BrO_3^-)(Br^-)(H^+)^2 \qquad (10)$$

Since the concentration of hydrogen ion remains constant throughout each experiment, this equation may be simplified to

$$dx/dt = k'(C - x)(D - 3x) + k''(C - x)(x), \text{ or}$$

$$\frac{dx/dt}{C - x} = Dk' + x(k'' - 3k'), \text{ where} \qquad (11)$$

$$k' = k_1(H^+), k'' = k_2(H^+)^2 \qquad (12)$$

and $C - x$, $D - 3x$ and x represent the concentrations in moles per liter of bromate ion, hydrogen peroxide and bromide ion, respectively.

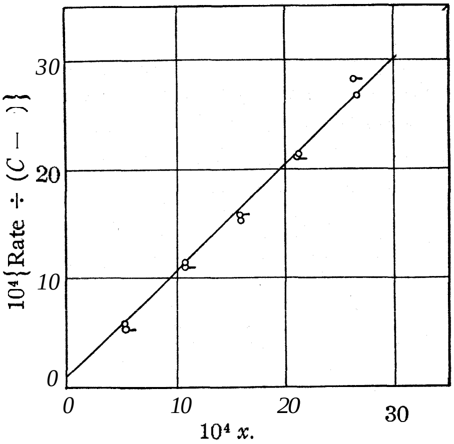

Fig. 2.—Evaluation of constants by use of Equation 11, Expts. 1A and 1B. Intercept = $1 \times 10^{-4} = 0.036k'$. Slope = $0.972 = k'' - 3k'$.

The form of Equation 11 suggested a method of evaluating the constants, namely, to determine rates by drawing tangents at a series of points on each x–t curve, to divide each rate by the corresponding concentration of bromate, and to plot these values of rate/bromate against x. If Equation 10 or 11 is correct, a straight line will result; the slope will be $k'' - 3k'$ and the intercept on the ordinate axis, Dk'. In applying this method tangents were drawn at points on the original oxygen–time curves by means of a tangentimeter,[8] kindly furnished by Dr. R. L. Hasche. These rates were changed to the unit, moles of bromide per liter per minute, and small corrections were applied for the bromide catalysis, $(k_3/6)(D - 3x)(x)(H^+)$.

The application of the method to Expts. 1A and 1B is shown in Fig. 2. The straight line corresponds to the values 98 and 0.028 for k_2 and k_1, respectively. The latter number is much smaller than any in Table I, but it is evident that the line in Fig. 2 could have been drawn to give a smaller intercept and, therefore, a still smaller value for k_1. On the other hand, since the line could not have a much greater slope than that shown, the value of k_2 has been determined within 2 or 3%. The method yielded definite slopes in the other experiments also, but the intercepts were relatively so small that k' (and k_1) could not be determined. Details will not

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[8] Latschow, This Journal, 47, 793 (1925).

be given since the values of k" — 3k' were entirely consistent with the constants determined by the method now to be described.

Integration of Equation 11 leads to the following

$$\log\left(\frac{x}{C-x}\right) = \log\left(\frac{\alpha}{C}\right) + \beta t, \text{ where} \tag{13}$$

$$\alpha = Dk'/(k'' - 3k') \text{ and } \beta = (Ck'' + (D - 3C)k')/2.303 \tag{14}$$

If these equations agree with the experimental data, a straight line will result when $\log [(x + \alpha)/(C - x)]$ is plotted against the time, t; the slope will be β and the intercept on the ordinate axis $\log (\alpha/C)$. Since both a and β involve k' and k", a method of approximations was employed in evaluating these rate constants. The ratio k'/k'' is always very small, and a is nearly negligible in comparison with x except in the early stages of each experiment. Accordingly Equation **13** was first tested by plotting $\log [x/(C - x)]$ againt t. Although $\log [x/(C - x)]$ is equal to minus infinity when x is zero,[9] it was found. as indicated by the dotted curves in Fig. 3,

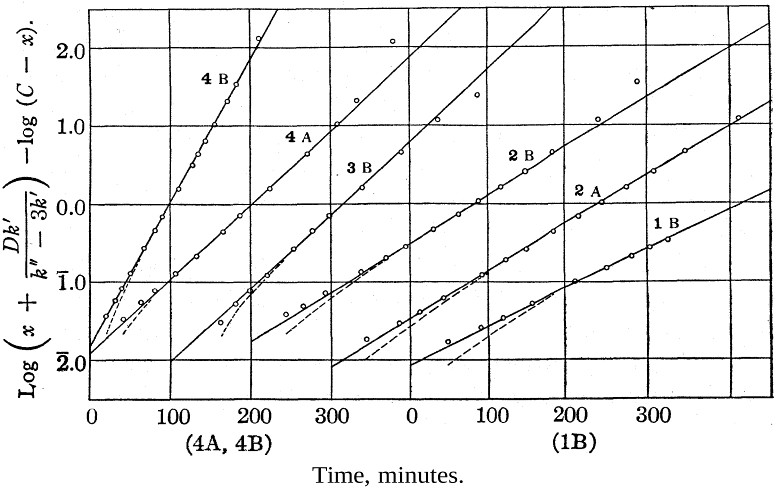

Fig. 3.—Evaluation of constants by use of Equation 13.

that each curve rapidly approached a straight line with increase in x. The slope and intercept of each line yielded values of β and a, as *a* first but close approximation in that experiment. $\mathrm{Log}\ (x + \alpha)/(C - x)$ was then plotted against t, another β, α pair was determined from the position of the new line, and the process was repeated when necessary. The values of k_1 and k_2 in Table IV correspond to the straight lines finally selected. However, other

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[9] Integration of $dx/dt = k(C - x)(x)$ leads to the equation $\log [(x + x_0)/(C - x)] = \log (x_0/C) + tCk/2.303$, where x_0 is the initial value of x. It is evident that a "pure" autocatalytic reaction will never start unless x_0 has a finite value. Ostwald, "Lehrbuch der allgem. Chem.," 1902, Vol. **II**, Part 2, pp. 265–267, discussed in detail a hypothetical case in which x was formed in a second independent reaction. Our results furnish an actual example.

pairs of constants, properly chosen within the limits specified, would satisfy fairly well the actual data in each experiment.

TABLE IV

CONSTANTS EVALUATED BY USE OF EQUATION 13

Expt.	$k_1 \times 10^3$	k_2	μ(Table II)	k_2/γ^4_{HBr}
1A	30 ±1.5	98∓2	0.156	515
1B	26.5±1.5	98∓2	.162	515
2A	24.2±1.5	100∓2	.190	550
2B	25.7±1	101∓1	.190	555
3A	24 ±2	97∓2	.185	535
3B	23 ±5	76∓4	.365	585
4A	30 ±2	76∓1	.365	585
4B	48 ±2	65.6∓0.4	.545	580

The *times* at various values of x, ***calculated*** by means of Equations 13, 14 and 12 and the constants of Table IV, are shown in Table III. These correspond to the smooth curves in Fig. 1 and the straight lines in Fig. 3. The calculated times at low and high values of x are somewhat greater than the observed times in six of the eight experiments, but are less in the remaining two, Expts. 3A and 3B. If the results in these two experiments prove to be incorrect, then the differences in the remaining cases indicate that a little oxygen is formed in the first five minutes by catalytic decomposition of the peroxide, when the bromide concentration, x, is very small; and that the values of x are slightly less than we have assumed. At the present time, however, we are not justified in rejecting Expts. 3A and 3B; and the differences at low and high values of x may be considered to be due to accidental errors in the zero setting of the oxygen buret and to correspond to the initial discrepancies referred to in Footnote 5. Corrections in x would greatly diminish the differences between calculated and observed times; the values of k_2 would not be changed appreciably, and those of k_1 would be altered by only a few per cent., being increased in Expts. 3A and 3B and decreased in the remaining cases. Thus in Expt. 2A, when x was decreased by 10^{-4}, the differences between calculated and observed times were found to be negligible throughout the experiment when k_1 and k_2 were assigned the values 0.022 and 100, respectively.

The value of k_2 is 99 ± 2 in the five experiments at ionic strengths between 0.156 and 0.19, but is much smaller in the three remaining experiments where the ionic strength is two or three times as great. This is in qualitative accord with Brönsted's theory of reaction rates,[10] which requires $k_2/\gamma^2_{HBr}\,\gamma^2_{HBrO_3}$ to be a true constant in dilute solutions. A definite test of this law is not possible on account of the lack of, or uncertainties in, the activity coefficients of bromie and hydrobromic acids in

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[10] (a) Bronsted, Z. *physik. Chem.*, 102, 169 (1922); *(b) ibid.*, 115, 337 (1925); *(c)* "The Velocity of Ionic Reactions," Columbia University Press, 1927.

the presence of sulfuric acid. Our results are in reasonable agreement with those of Skrabal and Weberitsch.[7]

The values of k_1 do not show the expected decrease with increasing ionic strength. The result is within ±15% of 0.026 in seven experiments, but is much greater in the last experiment at the highest ionic strength. It therefore, seems possible that another term should be added to Equation 10. If there is such an additional reaction, it is appreciable only at low concentration of bromide ion and high concentration of hydrogen ion. We may, therefore, conclude that, with this possible exception (and after making the small correction for bromide catalysis), the kinetic data are accurately represented by Equation 10.

In the two independent reactions of Equation 10 the following rate-determining steps are possible, or even probable

$$BrO_3^- + H^+ + H_2O_2 = X = HBrO_2 + H_2O + O_2 \qquad (15)$$

$$BrO_3^- + 2H^+ + Br^- = Y = HBrO_2 + HBrO \qquad (16)$$

where X and Y are critical complexes, as postulated by Brönsted.[10] The products shown in these equations are those usually assumed in bromate and bromide reactions.[11] The later steps will then involve a number of reactions such as the following, each of which must have a relatively high specific reaction rate

$$HBrO_2 + H_2O_2 = HBrO + H_2O + O_2 \qquad (17)$$

$$HBrO + H_2O_2 = H^+ + Br^- + H_2O + O_2 \qquad (18)$$

$$HBrO_2 + Br^- + H^+ = 2HBrO \qquad (19)$$

Equation 1 is the sum of Equations 15, 17 and 18; of 16, 17 and 18 (counted twice); and of 16, 19 and 18 (counted three times).

Summary

The autocatalytic reaction is accurately represented by the equation $BrO_3^- + 3H_2O_2 = Br^- + 3H_2O + 3O_2$ in dilute solutions when the concentration of hydrogen ion is less than 0.4 N. The catalytic decomposition of hydrogen peroxide due to bromide ion is appreciable only toward the end of the reaction.

The rate of the reaction at 25° in the dark was studied by measuring the volume of oxygen evolved. The results agreed closely with the assumption of two independent reactions

$$-d(BrO_3^-)/dt = k_1(BrO_3^-)(H_2O_2)(H^+) + k_2(BrO_3^-)(Br^-)(H^+)^2$$

where k_1 and k_2 have the values 0.026 ± 15% and 99 ± 2% in 0.12 N sulfuric acid.

Methods of evaluating the specific reaction rates k_1 and k_2 are discussed. A mechanism is suggested.

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[11] Cf. the "primary" reactions suggested by Bray, *Z. physik.* Chem., 54, 467, 490, 560 (1906).

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

THE CRISTOBALITE LIQUIDUS IN THE ALKALI OXIDE-SILICA SYSTEMS AND THE HEAT OF FUSION OF CRISTOBALITE

BY F. C. KRACEK

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It is desirable to know the exact course of the cristobalite liquidus curves for alkali silicate mixtures rich in silica, for two principal reasons. The first, and the more important practical reason, is that these curves might be expected to furnish a basis for the calculation of the heat of fusion of cristobalite, a quantity which has not yet been measured directly in the calorimeter. The second reason is of a theoretical nature and arises from a generalization based on the periodic table. Liquid immiscibility occurs in certain silicate mixtures rich in silica, as shown by Greig;[1] on recalculation, his results for the alkaline earth silicate mixtures in mole per cent. indicate a decreasing extent of immiscibility from MgO to SrO, that is, in the order of increasing basicity of the alkaline earth oxides. Barium silicate mixtures show no immiscibility, but present on the other hand a characteristic type of reverse S cristobalite melting curve. Owing to the great basicity of the alkali oxides, little or no immiscibility is to be expected in alkali silicate preparations, and, if found, it should be expected to decrease rapidly in the order of increasing atomic weights of the alkalies.

The papers hitherto published from this Laboratory dealing with alkali silicate systems[2] indicate that no liquid immiscibility occurs in sodium or potassium silicate mixtures at the cristobalite liquidus. The present paper deals with an extension of the study to all the alkali silicate systems in this region of temperatures. The results show that no liquid immiscibility exists in these systems, but that the two alkalies of lowest atomic weight, lithium and sodium, give rise to the reverse S type of melting point curve, which still persists slightly in the case of potassium; rubidium and cesium on the other hand give nearly ideal curves,[3] coincident when the composition is expressed in mole per cent. of the component oxides. The coincidence of the curves for rubidium and cesium lends itself to the interpretation that their slope is very nearly ideal at 100% silica, and they are accordingly employed in the calculation of the heat of fusion of cristobalite.

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[1] J. W. Greig, Am. J. *Sci.*, 13, 1 (1927).

[2] (a) Morey and Fenner, THIS JOURNAL, 39, 1173 (1917); (b) Morey and Bowen, "The Binary System Sodium Metasilicate–Silica," J. Phys. Chem., 28, 1167 (1924); (c) Kracek, Bowen and Morey, "The System K_2SiO_3–SiO_2," *ibid.*, 33, 1857 (1929).

See also (d) Jaeger and van Klooster, "On the Compounds of Lithium Oxide and Silica" Proc. Acad. *Sci. Amsterdam.* 16,857 (1914).

[3] J. H. Hildebrand, Proc. *Nat. Acad.*, 13, 267 (1927).

Experimental Part

1. Materials.—The preparations employed were made from the Laboratory stock of quartz, which was converted into cristobalite before adding the alkali. Decomposition with hydrofluoric and sulfuric acids gave a residue of 4.5 mg. on a 10-g. sample. Lithium, sodium, potassium and rubidium were in the form of carbonates. Each gave the theoretical factor on conversion to nitrate and sulfate, within close limits. Cesium was available in the form of the hydroxide,[4] which was converted to the nitrate for ease in weighing. To obviate excessive loss of cesium by volatilization, pure ammonium carbonate was mixed in excess with the nitrate and silica and carefully sintered at about 250 to 300° preliminary to fusion.

2. Preparation of Mixtures.—The required amounts of cristobalite and the alkali salt were weighed out, thoroughly mixed and sintered to drive off carbon dioxide (or carbon dioxide and nitrogen pentoxide in the case of cesium) over a Méker burner. The sintered mass was crushed and ground several times, with sintering intervening between crushings, to insure a uniform distribution of alkali in the mixtures. There was no appreciable loss of alkali under these conditions. The mixtures were sufficiently homogeneous. The composition was checked by evaporation with hydrofluoric acid, followed usually by fuming with sulfuric acid with the addition of ammonium carbonate.

3. Melting Point Determinations.—These were made by the now familiar quenching method of Shepherd and Rankin,[5] in conjunction with microscopic examination, using a cascade furnace wound with platinum–rhodium wire on the inner tube, and iridium-free furnace platinum wire on the outer tube. The furnace was controlled by the Wheatstone bridge type of regulator[6] with satisfactory constancy of the high temperatures required.

The temperatures were read by means of a Pt vs. 90 Pt–10 Rh thermocouple, using a Feussner type Wolff potentiometer and a highly sensitive galvanometer. The thermocouple was checked frequently at the melting point of palladium, and showed very little deterioration with use, probably because of the absence of iridium in the materials of the furnace. Day, Sosman and Allen's[7] value (1549 5°) for the melting point of palladium and Adams'[8] tables were used in the conversion of e. m. f. into degrees Centigrade.

4. The experimental results obtained are collected in Table I, giving the composition in weight and mole per cent. of silica calculated on the basis of the component oxides, and the results of critical quenches on each preparation. The preparations were held at constant temperature for about twenty minutes, long enough to insure equilibrium in each case, at the prevailing high temperatures.

Discussion

1.—The results are shown graphically in Fig. 1, plotting the reciprocal of the absolute temperature against the logarithm of the mole per cent. of silica, assuming 1713° for the melting point of cristobalite.[9] This type of plot was selected for theoretical reasons in order to facilitate the calculation of the heat of fusion of cristobalite, considered in the next section. Scales

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[4] Kindly furnished by my colleague, G. W. Morey.

[5] Shepherd and Rankin, *Am. J. Sci.*, 28,293 (1909).

[6] H. S. Roberts, J. Wash. *Acad. Sci.*, 11, 401 (1921).

[7] Day, Sosman and Allen, "High Temperature Thermometry," Carnegie Inst of Washington, Publ. 157.

[8] L. H. Adams, THIS JOURNAL, 36, 65 (1914); "International Critical Tables," Vol. I, 1926, p. 58.

[9] Ferguson and Merwin, *Am. J. Sci.*, 46,417 (1918); J. W. Greig, Ref. 1, p. 1436.

of temperature and mole per cent. of silica have been added for ready visualization of the various systems.

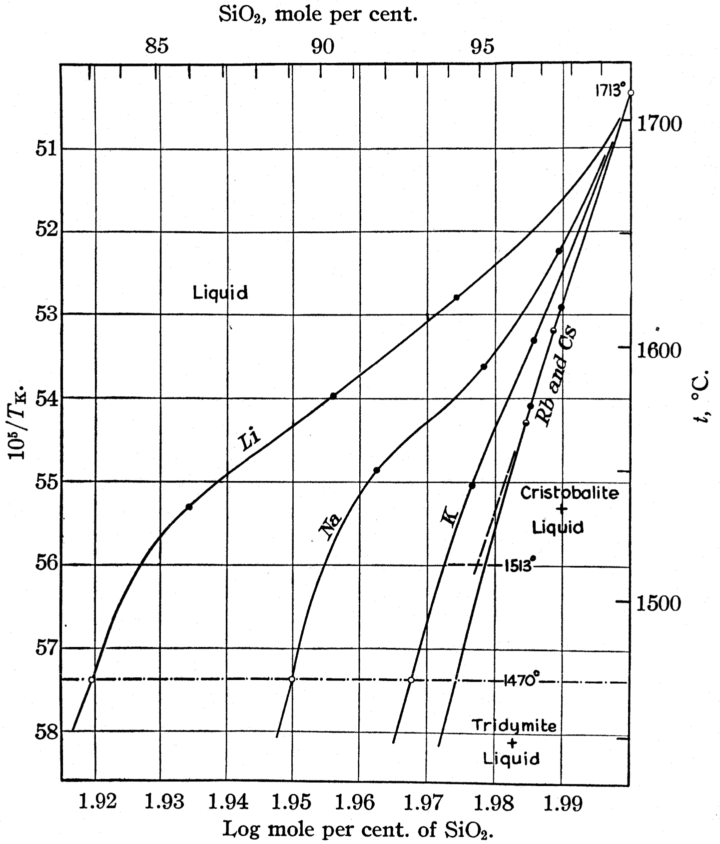

Fig. 1.—Cristobalite melting point curves for alkali silicate mixtures, plotting $1/T$ *vs.* log mole per cent. of SiO_2, with direct temperature and mole per cent. scales appended. Note the progressive change in the contour of the curves, and the coincidence of the curves for Rb and Cs.

TABLE I

RESULTS OF MELTING POINT DETERMINATIONS

No. of prepn.	Percentage of SiO_2 wt.	Percentage of SiO_2 mole	Temp., °C.	Time, min.	Microscopic examination
	A. Li_2O–SiO_2 mixtures. (Li_2O = 29.88, SiO_2 = 60.06)				
621	92.48	85.95	1529	20	Cristobalite + glass
			1535	20	Glass + very rare cristobalite
			Liquidus 1535°		
622	94.96	90.36	1566	20	Cristobalite + glass
			1581	20	Very rare cristobalite + glass
			1583	20	Glass
			Liquidus 1581°		

TABLE I *(Concluded)*

No. of prepn.	Percentage of SiO_2 wt.	mole	Temp., °C.	Time, min.	Microscopic examination
623	97.01	94.17	1607	20	Cristobalite + glass
			1621	20	Rare cristobalite + glass
			1624	20	Glass
			Liquidus 1622°		
	B. Na_2O-SiO_2 mixtures. (Na_2O = 61.99, SiO_2 = 60.06)				
566	91.46	91.79	1541	20	Cristobalite + glass
			1550	20	Rare cristobalite + glass
			1554	20	Glass
			Liquidus 1551°		
567	95.00	95.13	1592	20	Rare cristobalite + glass
			1595	20	Glass
			Liquidus 1593°		
568	97.50	97.57	1639	20	Cristobalite + glass
			1643	20	Rare cristobalite + glass
			1646	20	Glass
			Liquidus 1644°		
	C. K_2O-SiO_2 mixtures. (K_2O = 94.19, SiO_2 = 60.06)				
286	92.01	94.76	1541	20	Cristobalite + glass
			1544	20	Rare cristobalite + glass
			1547	20	Glass
			Liquidus 1544°		
287	95.00	96.75	1599	20	Cristobalite + glass
			1602	20	Rare cristobalite + glass
			1607	20	Glass
			Liquidus 1603°		
	D. Rb_2O-SiO_2 mixtures. (Rb_2O = 186.88, SiO_2 = 60.06)				
506	89.86	96.50	1559	20	Cristobalite + glass
			1567	20	Rare cristobalite + glass
			1571	20	Glass
			Liquidus 1569°		
507	92.35	97.41	1604	20	Rare cristobalite + glass
			1609	20	Glass
			Liquidus 1607°		
	E. Cs_2O-SiO_2 mixtures. (Cs_2O = 281.6, SiO_2 = 60.06)				
151	86.03	96.65	1560	20	Cristobalite + glass
			1574	20	Rare cristobalite + glass
			1578	20	Glass
			Liquidus 1575°		
152	89.90	97.66	1613	20	Cristobalite + glass
			1615	20	Cristobalite + glass
			1618	20	Glass
			Liquidus 1617°		

It is seen that Li_2O-SiO_2 and Na_2O-SiO_2 mixtures present pronounced reverse S melting point curves of cristobalite. With K_2O-SiO_2 mixtures the curvature is greatly reduced, and the curve becomes normal with Rb_2O-SiO_2 and Cs_2O-SiO_2.

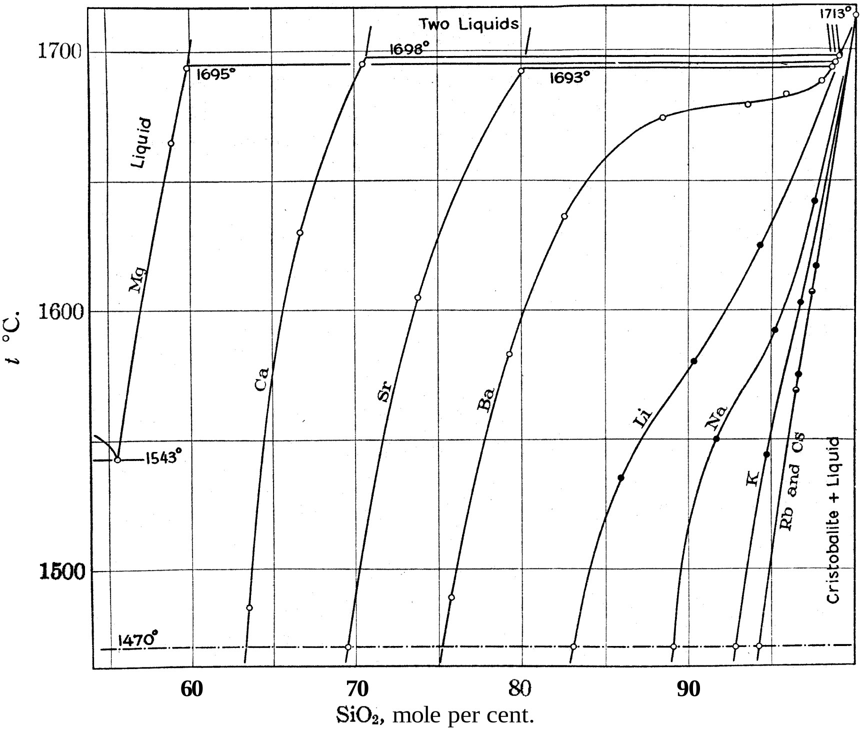

Fig. 2.—Diagram to illustrate the periodicity of the cristobalite melting point curves for the alkaline earth and alkali silicate mixtures. Full circles denote results of this investigation. Open circles taken from work published by this Laboratory. The curve for Ra would be found between Ba and Li, if Ra mixtures could be studied.

To bring out clearly the periodic progression in the change of type of melting point curves of cristobalite, the data for the alkaline earths and alkalies have been collected in Fig. 2. The experimental data[10] for the alkaline earths have been recalculated to mole per cent. on the basis of the component oxides. The black circles represent values obtained in the present investigation. The periodic relationship is obvious from the figure and need not be further enlarged upon.

2. Heat of Fusion of **Cristobalite.**—The available information on this subject has been critically considered by Sosman,[11] who comes to the con-

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[10] J. W. Greig, Ref. 1; Bowen and Andersen, *Am. J. Sci.,* **37, 487 (1914);** P. Eskola, *ibid.,* **4,331** (1922).

[11] R. B. Sosman, "The Properties of Silica," The Chemical Catalog Co., Inc., New York, 1927, pp. 310–359.

clusion that the heat of fusion of cristobalite is of the order of 20 cal./g. This quantity is not easily amenable to direct measurement, and Sosman's estimate has been derived from Wietzel's[12] work on the differences between the heat of solution of cristobalite and of fused silica in hydrofluoric acid. Washburn[13] and Sosman[14] employed the eutectic in the system Al_2O_3–SiO_2. Washburn's value was based on an approximate location of the eutectic and is obviously too high. Sosman employed Bowen and Greig's[15] figures for the eutectic and obtained a value (25.9 cal./g.) somewhat smaller than that calculated in this paper. If a point on the cristobalite liquidus (3.01 mole per cent. of Al_2O_3, 1615°) is used for the calculation, the result is 38.7 cal./g.

Inspection of Fig. 1 shows that the cristobalite liquidus $1/T$ vs. log mole per cent. of silica curve is very nearly straight for at least 100° below the melting point of cristobalite in the Rb_2O–SiO_2 and Cs_2O–SiO_2 systems. This straight line was produced to 1513°, where the melting point lowering, ΔT, is 200°. The corresponding value of log mole per cent. of SiO_2 = 1.9774. Applying the Schröder–Le Chatelier[16] formula for ideal solubility in the form

$$L_f = \frac{4.578\ T\ T_0}{\Delta T} \log \frac{X_0}{X}$$

where L_f is heat of fusion, T_0 is absolute melting point of cristobalite, 1986°K., T is $1513 + 273 = 1786$°K. and $\log X_0/X = 2 - 1.9774 = 0.0226$, the value 1835 cal./mole or 30.5 cal./g. is obtained.

This calculation is made on the basis of the moles of the component oxides present in the mixtures, as has already been stated, rather than on the assumption of the existence of definite compounds in the melts. It is not improbable that compound formation does take place to some extent in these melts, even at the temperatures of the cristobalite liquidus, but since silicates are essentially additive compounds whose dissociation increases with rising temperatures, and since even the metasilicates of the alkalies are considerably dissociated at their melting points,[17] it seems reasonable to suppose that no important amount of any alkali silicate is present at the temperatures and compositions in question. This assumption gains some weight on consideration that silica behaves as a non-polar liquid (dielectric constant at 25° = 3.2 to 3.9) at high temperatures, in its tendency to form two liquid layers with many highly polar oxides in solution.

Many physical constants of silica have apparently anomalous values, and in this respect the heat of fusion of cristobalite forms no exception. The

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[12] R. Wietzel, Z. *anorg. allgem. Chem.*, 116, 71 (1921).

[13] E. W. Washburn, *J. Am. Ceram. Soc.*, 2, 1007 (1919).

[14] R. B. Sosman, Ref. 11, p. 358.

[15] Bowen and Greig, *J. Am. Ceram. Soc.*, 7, 238 (1924).

[16] I. Schroder, *Z. physik. Chem.*, 11, 449 (1893); H. Le Chatelier, *Compt. rend.*, 118, 638 (1894).

[17] Morey and Bowen, *J. Phys. Chem.*, 28, 1167 (1924).

ratio of the molar heat of fusion to the absolute melting point, L_f/T_0 for cristobalite, $1835/1986 = 0.924$ is exceptionally small, and falls below that of the normal (non-polar) substances carbon tetrachloride (2.49) and methane (2.58).

3. Concluding Remarks.—The errors in the determinations given in this paper are estimated to be within 0.10% interval in composition and a 5° interval in temperatures based on the scale used in this Laboratory. This precision is possible, and can be exceeded, principally through the use of the static method of quenching[5] and its attendant technique, which makes it possible to attain equilibrium in the sample at each point, and hence does not depend upon heat effects or the velocity of formation or solution of crystals, characteristic of dynamic methods of melting point determination. It would be idle to claim that high precision is always attained in quenching work, nor is it always aimed at. In many cases crystals grow or dissolve very slowly, or the melt may be so viscous that diffusion of the dissolved material into the melt takes place extremely slowly; in other cases moderate precision suffices to establish the course of a curve within close enough limits. In the present instance comparison may be made with the results of Morey and Bowen[2b] for the system Na_2SiO_3–SiO_2 and of Kracek, Bowen and Morey[2c] for the system K_2SiO_3–SiO_2. In each of these systems one point had been established on the cristobalite liquidus, namely, at 4.07 wt. per cent. of Na_2O, 1596°, and at 4.5 wt. per cent. of K_2O, 1638'. The point in the Na_2O system lies practically upon the newly determined curve, while that in the K_2O system lies above the curve, which is found to pass through 1627' at the given composition. The agreement is considered adequate in view of the fact that only moderate accuracy was attempted in locating the latter point.

It is hoped that the results given in this paper will help in gaining a wedge with which to attempt to open the question of the chemical behavior and nature of silica. It seems assured that vitreous silica behaves as a fairly normal, non-polar liquid of comparatively low ionizing power at high temperatures, judging from the results obtained; data on the conductivity of vitreous silica itself are, however, of such conflicting nature that no conclusions can be drawn from them respecting vitreous solutions.

Summary

The melting point curves of cristobalite in silica-rich mixtures of Li_2O, Na_2O, K_2O, Rb_2O and Cs_2O with SiO_2 have been determined and the characteristics of these curves have been discussed.

The heat of fusion of cristobalite has been calculated as 30.5 cal./g. from the melting point lowering of cristobalite by Rb_2O and Cs_2O.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. VII. THE OXIDATION OF HYDROQUINONE BY CERIC SULFATE

BY N. HOWELL FURMAN AND JOHN H. WALLACE, JR.

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Introduction

A number of uses of ceric sulfate in volumetric analysis have recently been described in previous papers of this series,[1] and in those of other investigators.[2] In this communication we present a study of the direct volumetric determination of hydroquinone with standard ceric sulfate, both by the potentiometric method and with diphenylamine or methyl red as color indicator, We have compared this new method with methods which have been described previously.

Valeur,[3] Sorensen and Linderström–Lang[4] and Kolthoff[5] have studied the iodimetric determination of hydroquinone. Our experience is in accord with that of Kolthoff, who suggested that the iodimetric method is best applied by adding an excess of iodine, then bringing the hydrogen-ion concentration of the solution below 5×10^{-6}, in order that the oxidation of the hydroquinone to quinone shall be quantitative. The excess of iodine is then determined with standard arsenite solution, rather than with thiosulfate, as Sorensen and Linderstrom–Lang suggested.

Kolthoff[5] also studied the reaction between hydroquinone and dichromate in strong acid solution; he found that the oxidation was quantitative and that the end-point may be determined potentiometrically with a platinum gauze as indicator electrode; the gauze is heated to redness before each titration. The end-point may also be determined by using diphenylamine as an internal indicator.

We have found that the reaction

$$2Ce(SO_4)_2 + C_6H_4(OH)_2 = C_6H_4O_2 + H_2SO_4 + Ce_2(SO_4)_3, \text{ or}$$
$$2Ce^{++++} + C_6H_4(OH)_2 = C_6H_4O_2 + 2H^+ + 2Ce^{+++}$$

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[1] Furman, THIS JOURNAL, 50, 755, 1676 (1928); Furman and Evans, *ibid.*, 51, 1128 (1929); Furman and Wallace, *ibid.*, 51, 1449 (1929).

[2] Martin, *ibid.*, 49, 2133 (1927); Willard and Young, *ibid.*, 50, 1322, 1334, 1368, 1372, 1379 (1928); *Ind. Eng. Chem.*, *20*, 972 (1928); THIS JOURNAL, 51, 139, 149 (1929); I. A. Atanasiu, *Bull. Soc. Roum. Chem.*, 30, 1 (1928); Atanasiu and V. Stefanescu, *Ber.*, 61, 1343 (1928); Rathsberg, *ibid.*, 61, 1664 (1928); Someya, *Z. anorg. allgem. Chem.*, 181, 183 (1929); Soule, THIS JOURNAL, 51, 2117 (1929); Berry, *Analyst*, 54, 461 (1929).

[3] Valeur, *Bull. soc. chim.*, 23, 58 (1900).

[4] Sörensen and Linderström–Lang, *Compt. rend. trav. lab. Carlsberg*, 14, No. 14 (1921).

[5] Kolthoff, *Rec. traa. chim.*, *45*, 745 (1926).

is not only quantitative, but is superior in many respects to the other reactions which have been used for the quantitative determination of hydroquinone. The reaction is rapid at room temperature, and the titrations may be made directly. The potentiometric and diphenylamine end-points are much sharper than is the case when dichromate is used. A bright platinum wire serves as indicator electrode, and we failed to detect electrode poisoning in the ceric sulfate reaction. Methyl red[6] also serves as an indicator if it is added near the end-point. The red color is destroyed by a slight excess of ceric sulfate. Our observations have been made with solutions of hydroquinone which contained various concentrations of sulfuric or hydrochloric acid.

Experimental

The apparatus has been described in previous papers of this series; a bright platinum wire and a normal calomel half-cell made up the electrode system.

The ceric sulfate solutions were prepared by dissolving commercial rare earth oxides in enough dilute sulfuric acid to make the solution 1 N in acid when diluted until 0.1 N in oxidizing powder. After standing until clear (a week or more), the solutions were filtered and were found to be stable. The ceric solutions were standardized potentiometrically against pure sodium oxalate or pure arsenious oxide. In the latter case iodine monochloride was used as a catalyst.[7]

Hydroquinone solutions were prepared by dissolving pure hydroquinone in water containing 10 cc. of 6 N sulfuric acid and diluting to a liter. They were kept in smooth bottles of amber glass and were found to be stable over a period of at least eight hours. The solutions were standardized by adding an excess of standard iodine, and titrating back with standard arsenite solution, using starch as an indicator. The sodium bicarbonate was added after an excess of iodine had been added to the hydroquinone solution.

Diphenylamine was used in 1% solution in sulfuric acid. The methyl red solution contained 0.2 g. of methyl red in 100 cc. of 1.2 N sulfuric acid.

Titration of Hydroquinone with Ceric Sulfate. (a) **Potentiometric.**—Measured portions of hydroquinone solutions were diluted to 100 cc. after adding acid. The nature and concentration of the acid and the rate of addition of the ceric sulfate were not found to be important factors. All titrations were made at room temperature. The results are summarized in Tables I and II.

The potentiometric titration gives a curve rising regularly and gradually from a value between 0.2 and 0.3 volt (Pt vs. N calomel electrode) to be-

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[6] Rathsberg, Ref. 2, used methyl red as indicator in the oxidation of trivalent antimony with ceric sulfate.

[7] Willard and Young, THIS JOURNAL, 50, 1368 (1928).

TABLE I

POTENTIOMETRIC TITRATION OF 0.09357 N HYDROQUINONE WITH 0.1179 N CERIC SULFATE

Concn. due to acid added		None	0.75 N H_2SO_4	1.5 N H_2SO_4	0.5 N HCl	1.5 N HCl	2 N H_2SO_4
Hydroquinone, cc.		25	25	25	25	25	50
Ceric sulfate	Calcd., cc.	22.66	22.66	22.66	22.66	22.66	45.32
	Found, cc.	22.65	22.63	22.66	22.65	22.67	45.28
	Error, cc.	−0.01	−0.03	±0.00	−0.01	$0.01	−0.04

TABLE II

POTENTIOMETRIC TITRATION OF 0.0914 N HYDROQUINONE WITH 0.1095 N CERIC SULFATE

Concn. of acid added		None	None	None	1 N H_2SO_4	2 N H_2SO_4	1 N HCl	2.5 N HCl
Hydroquinone, cc.		10	25	50	10	10	10	25
Ceric sulfate	Calcd., cc.	8.35	20.88	41.76	8.35	8.35	8.35	20.88
	Found, cc.	8.34	20.91	41.79	8.35	8.37	8.35	20.88
	Error, cc.	−0.01	+0.03	$0.03	−0.02	+0.02	±0.00	±0.00

tween 0.4 and 0.5 volt as the end-point is approached. The voltage rise at the end-point is of the order of 0.25–0.35 volt per drop (0.05 cc.) of ceric sulfate. The following are some typical values for a titration

Cc. ceric soln.	0.00	20.00	40.00	44.00	45.50	44.57	44.61	44.65
E. m. f.	0.285	0.371	0.404	0.435	0.459	0.583	0.848	0.900

There is an obvious maximum between 44.57 and 44.61 cc. of reagent. The reaction proceeded rapidly at all concentrations of acids that were used and the potential became steady almost immediately.

The reaction was tested further by using pure recrystallized hydroquinone as a standard substance both for ceric sulfate and for iodine. The general conditions were analogous to those which have been described (Tables I and II).

Ceric sulfate was standardized against pure sodium oxalate: found, 0.1073 N, average of 0.1072, 0.1074, 0.1073 N. Hydroquinone was then used as a standard substance.

Hydroquinone, g.	0.2638	0.2539	0.2056	0.1863	0.2570	0.2196
Ceric soln., cc.	44.55	43.01	34.81	31.55	43.53	37.23
Normality	0.1076	0.1073	0.1074	0.1073	0.1073	0.1072

These determinations, if interpreted as analyses of hydroquinone with 0.1073 N ceric sulfate, give 99.7, 100.01, 99.95, 99.98, 100.00 and 100.09% of hydroquinone, respectively.

Iodine solutions were standardized directly against weighed samples of pure arsenious oxide (U. S. Bureau of Standards), and then against hydroquinone by adding an excess of the iodine solution and titrating back with standard arsenite, prepared from the pure arsenious oxide.

Iodine Solution I, Normality

Against As_2O_3.....	0.1002, 0.1001, 0.0999, 0.1002, 0.1001, 0.1002	**Av.** *0.1001*
Hydroquinone.....	0.1002, 0.1002, 0.1001, 0.0999, 0.1002	**Av.** *0.1001*

Iodine Solution II, Normality

Against As_2O_3......	0.0996, 0.0998, 0.0996, 0.0997, 0.0997	**Av.** *0.0997*
Hydroquinone.....	0.0998, 0.0999, 0.0996, 0.0999 0.0996, 0.0998, 0.0997	**Av.** *0.0998*

The foregoing determinations appear to have established the quantitative nature of the reaction between hydroquinone and ceric sulfate. The use of diphenylamine or methyl red as indicators was then tried, and the potentiometric values were assumed to be correct.

(b) Diphenylamine as Indicator.—If **0.05** cc. of a 1% solution of diphenylamine in sulfuric acid is added to the hydroquinone solution, the end of the oxidation of the latter is indicated by the sudden appearance of the blue oxidation product of the diphenylamine. We have found that a correction of 0.05 cc. is to be subtracted from the volume of ceric solution to bring the results into agreement with the potentiometric values, as shown in Table III.

TABLE III

TITRATION OF HYDROQUINONE USING DIPHENYLAMINE AS INDICATOR

Initial volume	*100*	*100*	*100*	*200*	*150*	*50*
Concn. of acid added	**None**	*1 N* H_2SO_4	*2 N* H_2SO_4	*1 N* HCl	*2 N* HCl	**None**
Cc. of hydroquinone	*25*	*25*	*25*	*25*	*25*	*25*
Ceric soln. used (uncorr.), cc.	*20.96*	*20.95*	*20.97*	*20.96*	*20.98*	*20.96*

The average of three potentiometric determinations gave **20.92** cc. of ceric solution equivalent to **25** cc. of the hydroquinone.

(c) Methyl Red as Indicator.—We have found that methyl red may be used successfully as an indicator in this reaction. As soon as the hydroquinone has been oxidized, the ceric sulfate destroys the red color of the indicator. Because of the color of the quinone that is formed, the end-point change is from deep orange to yellow. It is well to add the methyl red within about a cubic centimeter of the end of the titration. Two drops of 0.2% solution are necessary for a good color change. We have found that methyl red is a less satisfactory indicator in this titration than diphenylamine.

Some results are presented in Table IV. In each case **25** cc. of hydro-

TABLE IV

TITRATION OF HYDROQUINONE USING METHYL RED AS INDICATOR

Initial volume, cc.	*50*	*75*	*100*	*150*	*200*
Concn. of acid added	**None**	1.5 *N* H_2SO_4	1 *N* HCl	1 *N* H_2SO_4	*2 N* HCl
Ceric sulfate used, cc. (uncorr.)	*20.93*	*20.94*	*20.95*	*20.93*	*20.92*

quinone was titrated and the average requirement was **20.92** cc. of ceric sulfate by the potentiometric method.

It is evident that there is practically no correction required in this case (**0.1** N ceric solution).

The Reverse Titration.—A brief study was made of the titration of ceric sulfate with hydroquinone. The general procedure was as has been described, and the end-point was determined potentiometrically. It was first found potentiometrically that 25 cc. of hydroquinone solution was equivalent to **25.91** cc. of ceric sulfate (average of several titrations with ceric sulfate). The results are presented in Table V.

TABLE V

TITRATION OF CERIC SULFATE WITH HYDROQUINONE

	Initial concn. of H_2SO_4	0.75 N	1 N	1.2 N	1.5 N	2.5 N
	Ceric solution, cc.	25	50	25	25	25
Hydroquinone	Calcd., cc.	24.13	48.26	24.13	24.13	24.13
	Found, cc.	24.12	48.24	24.15	24.14	24.14
	Error, cc.	−0.01	−0 02	+0.02	+0.01	fO.O1

These results indicate that the titration is fully as exact as the reverse process and that, in strong contrast with permanganate, a moderate excess of ceric sulfate does not attack quinone.

A few experiments proved that the isomers of hydroquinone, namely, resorcinol and catechol were oxidized farther than their quinone stages; the reactions proceeded so sluggishly at room temperature that it was not possible to find a definite end-point.

In experiments not detailed here, we found that the determination of hydroquinone with dichromate was much less convenient than that with ceric sulfate, either by the potentiometric or diphenylamine method.

Summary

The reaction between **0.1** N solutions of hydroquinone and ceric sulfate has been shown to be stoichiometric, rapid and convenient, as contrasted with other volumetric methods which have been proposed for the determination of hydroquinone.

The titration may be made with either solution as reagent, using the potentiometric method of determining end-points.

When a standard solution of ceric sulfate is used, either diphenylamine or methyl red may be used as an internal indicator. In the former case the customary correction for ceric solution required to oxidize the diphenylamine must be deducted; with methyl red the correction is practically negligible. The diphenylamine color change is more satisfactory than that with methyl red.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA]

THE EFFECT OF TEMPERATURE ON THE MOLECULAR SURFACE ENERGY OF BINARY MIXTURES. II. WATER AND NICOTINE

BY W. F. SEYER AND A. F. GALLAUGHER

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A previous communication[1] embodied the results of surface tension measurements carried out upon mixtures of a polar and non-polar liquid, sulfur dioxide and benzene. The following pages contain the results of similar measurements made on mixtures of two polar liquids, water and nicotine. The investigation had a two-fold object: .to find the effect of temperature on the molecular surface energy of a binary mixture of two polar liquids both of which would ordinarily be assumed to be associated, and to find further evidence to support the theory of hydrate formation in the case of nicotine and water.

Nicotine dissolves in its own volume of water to form a sticky, viscous liquid, which on warming becomes turbid and separates into two liquid layers, the upper being a saturated solution of nicotine in water, and the lower a saturated solution of water in nicotine. Further warming will again bring about the formation of a single homogeneous phase. Ever since the discovery of the ring-shaped solubility curve of nicotine and water by Hudson,[2] attempts have been made to show the existence of hydrates at the temperatures below the lower critical temperature, hoping thereby to explain this peculiar phenomenon. The upper portion of the curve in Fig. 1, above the line AB, is similar in shape to that obtained whenever any two immiscible liquids are heated. In such cases complete miscibility occurs whenever the kinetic energy of the molecules of the liquids is sufficient to overcome the internal pressures. Solution in this case is obviously only a matter of diffusion. The portion of the curve below AB which defines the limits of complete miscibility has been quite generally ascribed to the existence of hydrates. These hydrates act in bringing about solution in a manner similar to that of alcohol when added to a two-phase ether–water system. If the temperature of a homogeneous solution containing equal amounts of water and nicotine is then raised to 61°, these supposed hydrates are decomposed and, as a consequence, the two phases make their appearance.

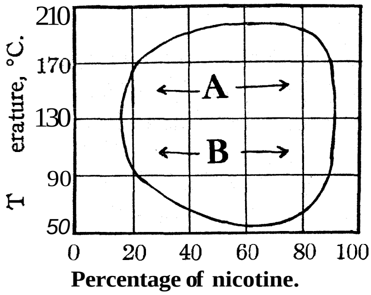

Fig. 1.

Considerable work has been done with the object of establishing the

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[1] Seyer and Peck, THIS JOURNAL, 51, 14 (1929).

[2] Hudson, Z. *physik.* Chem., 47,113–115 (1904).

existence of these hydrates. Owing to the viscous nature of the solutions at temperatures below 20°, it has so far been difficult to obtain reliable freezing point data and quite impossible to separate any hydrates which might have been formed. While Jephcott[3] upon an examination of the freezing points of solutions of nicotine found indications of hydrates, still, most of the evidence supporting the theory of hydrate formation has come from the investigation of other physical properties of nicotine and water solutions. Thus Tsakalotos[4] investigated the viscosity, Skalweit[5] the specific gravity, Winther[6] the index of refraction and specific rotatory power, all with a view toward offering an explanation of the closed solubility curve. Tsakalotos found the viscosity of various mixtures to be much greater than that calculated from the rule of mixtures, the curve for the coefficient of viscosity of the system showing a well-defined maximum at 78% concentration of nicotine. Skalweit observed that when water is added to nicotine, heat is produced and a diminution of volume takes place, and that the densities of the mixtures show a maximum at 72% nicotine

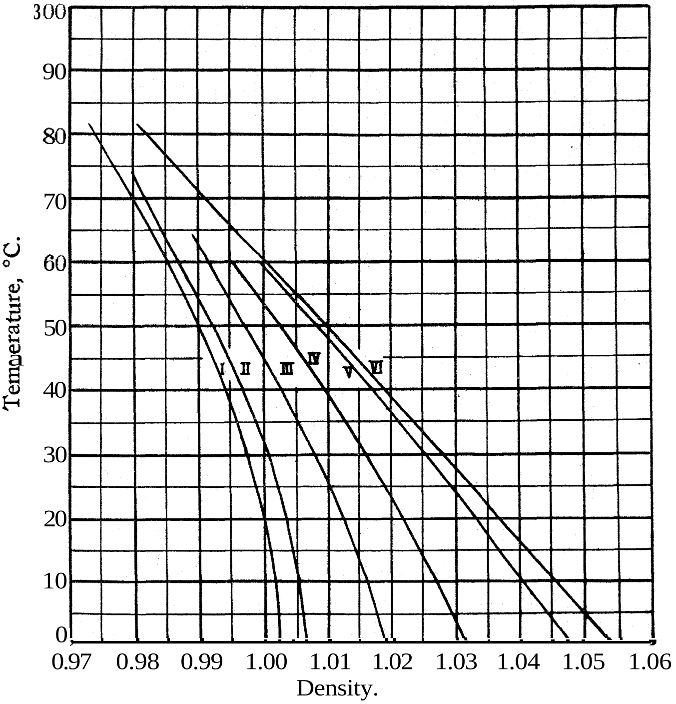

Fig. 2.

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[3] Jephcott, *J. Chem. Soc.*, 115,104 (1919).

[4] Tsakalotos, Bull. *soc. chim.*, *[4]* 5,397 (1909).

[5] Skalweit, *Ber.*, 14, 1809–1810 (1881).

[6] Winther, *Z. physik. Chem.*, *60, 563* (1907).

concentration. Jephcott points out that if the density or specific rotatory power of nicotine in aqueous solutions is plotted against concentration, a series of maxima is obtained. He also observed that the time required for equilibrium to be established at 40 and 80% nicotine was appreciable. The results of these various investigations seem to show the possibilities of hydrate formation at concentrations of about 40 and 80% nicotine. As will be shown later, the surface tension measurements of the solutions at different temperatures also support this view.

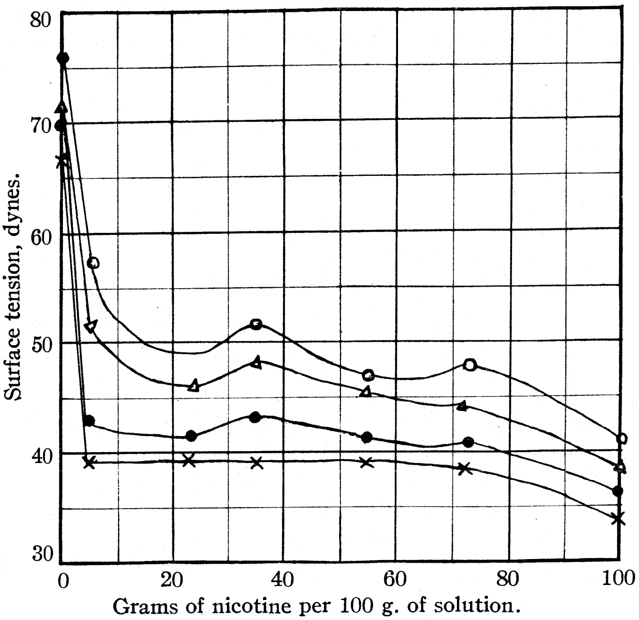


Fig. 3.—○, Curve for 0°; △, curve for 20°; ●, curve for 40°; ×, curve for 60°.

Determinations of Densities and Surface Tensions.—The method used for determining the densities of nicotine and its aqueous solutions was the same as that used for benzene and sulfur dioxide solutions below −10°. This required finding the loss in weight of a quartz sinker when weighed in the liquid.[1] The apparatus and technique involved in the surface tension measurements were also the same as formerly described. The readings were always made with a falling meniscus and in most cases a much longer time was required for the nicotine–water solutions to reach equilibrium than was the case with benzene–sulfur dioxide solutions, which was to be expected in view of the greater viscosities of the former solutions. In most cases it required from five to six hours before the readings became constant.

Preparation of Materials.—The nicotine was obtained from the Eastman Kodak Co. and had a boiling point of 115–117° at 12-mm. pressure.

As it could not be purified by recrystallization, it was redistilled several times under vacuum, the first and last portions of the distillates being rejected. In this way a fraction was obtained which distilled within one degree at 12-mm. pressure. To prevent oxidation the purified nicotine was kept in bottles that were completely filled as suggested by Jephcott, with the result that no coloration was discernible even after standing for several months. The water used in preparing the aqueous solutions was of the purity required for conductivity work. From these materials six solutions were prepared and kept in containers free from air until ready for use. The composition of the solutions is given in Table I.

TABLE I

COMPOSITION OF MIXTURES

Mixture	I	II	III	IV	V	VI
Nicotine/100 g. of soln., g.	5.35	10.12	23.74	35.15	54.86	72.16
Average molecular weight	18.91	...	23.55	26.13	35.08	50.17

The following series of tables contains the densities of nicotine and of nicotine–water solutions at different temperatures corrected to vacuum.

TABLE II. NICOTINE

Temp., °C.	Density[a]
−49.18	1.0616
−41.03	1.0556
−30.23	1.0473
−19.27	1,0385
−10.45	1.0318
− 0.85	1.0241
9.58	1.0159
19.27	1.0081
30.18	1.0001
49.49	0.9850
59.98	.9765
76.93	.9631
97.64	.9465
118.22	.9297
138.91	.9131
163.92	.8923
183.18	.8763
208.28	.8495

TABLE V. MIXTURE III

Temp., °C.	Density
0.40	1.0193
10.30	1.0163
19.90	1.0127
29.30	1.0082
40.20	1.0031
50.60	0.9970
61.40	9905

TABLE III. MIXTURE I

Temp., °C.	Density
3.10	1,0027
10.20	1.0024
20.20	1.0002
29.90	0.9975
40.10	.9939
51.20	.9894
60.50	.9847
70.80	.9793
75.40	.9768
79.60	.9741

TABLE VIII. MIXTURE VI

Temp., °C.	Density
1.00	1.0534
9.80	1.0462
19.40	1.0376
30.10	1.0280
40.10	1.0191
50.10	1.0100
60.20	1.0006
70.00	0.9914
75.90	0.9856

TABLE IV. MIXTURE II

Temp., °C.	Density
1.0	1.0070
10.27	1.0058
19.80	1.0036
30.70	1.0003
40.30	0.9967
50.60	.9919
59.70	.9873
69.80	.9817

TABLE VI. MIXTURE IV

Temp., °C.	Density
1.05	1.0313
10.20	1.0268
20.00	1.0216
30.40	1.0156
39.80	1.0095
50.30	1.0026
60.45	0.9951

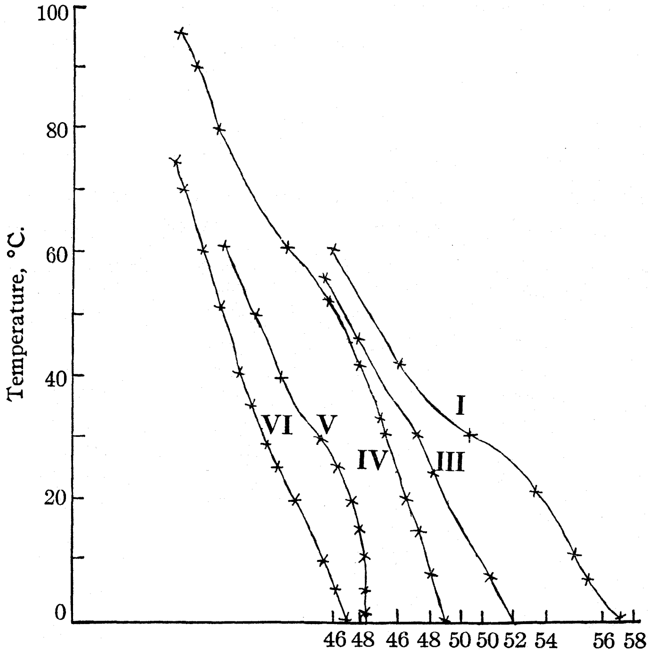
TABLE VII. MIXTURE V

Temp., °C.	Density
0.40	1.0474
10.20	1.0403
20.00	1.0330
29.80	1.0252
40.20	1.0167
50.40	1.0079
62.7	0.9974;

[a] Densities corrected to vacuum.

Figure 1 shows that with increasing nicotine concentration the temperature–density relationships become almost linear. The densities of the nicotine vary somewhat from those previously recorded, which is what might be expected in view of the great difficulty encountered in purifying nicotine.

The surface tension values were calculated by means of the formula $\gamma = KHd$ where γ is the surface tension in dynes, K a constant for the apparatus employed, H the corrected difference in height of liquid in the two capillaries and d the density of the solutions. Two surface tension tubes were employed whose constants were 15.026 and 18.482. In the case of the solutions so far examined the density of the vapor was so small as to be negligible. Since the surface tensions were determined at slightly different temperatures from that of the densities, it was necessary to interpolate to get the required densities, for the surface tension calculations. The Eotvos constant in the case of nicotine was obtained by plotting the molecular surface energies against temperatures on a large scale and then taking the differences of the molecular surface energies from the curves over intervals of about 30°. The total surface energies for certain temperatures have been calculated as well as the constant C in Macleod's[7] equation



Surface tension.

Fig. 4.

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[7] Macleod, *Trans. Faraday Soc.*, 29, 38 (1923–1924).

$\gamma = C(D - d)^4$ where γ is the surface tension, D the densities of the liquid and d the density of the vapor, from the surface tension directly. The surface tension and the other derived quantities are given in their accustomed units in the following tables.

TABLE IX
SURFACE TENSION AND OTHER DATA

Temp., °C.	Density	h corr.	Surface tension, dynes/cm.	Mol surface energy, ergs/sq. cm.	Eotvos constant, K_c	Total surface energy, ergs/sq. cm.	Macleod constant, C
−49.31	1.0627	2.37	46.58	1331		71.0	36.78
−39.55	1.0546	2.34	45.39	1307			37.00
−28.95	1.0465	2.29	44.12	1277			36.98
−19.09	1.0392	2.25	43.16	1244	2.5	70.0	37.86
− 9.19	1.0305	2.22	42.22	1227			37.78
0.75	1.0230	2.18	41.41	1206			37.78
11.41	1.0147	2.13	39.89	1174	2.6	69.9	37.61
20.55	1.0072	2.08	38.61	1141			37.52
30.19	1.0000	2.04	37.70	1121			37.70
39.83	0.9915	1.99	36.54	1092	2.7	70.9	37.77
51.01	.9837	1.94	35.37	1063			37.76
60.66	.9760	1.89	34.15	1032			37.64
70.86	.9665	1.85	33.08	1005	2.8	70.7	37.86
79.06	.9607	1.81	32.17	983			37.77
89.07	.9527	1.77	31.25	959			37.63
93.45	.9490	1.76	30.99	953	2.4	67.0	38.01

TABLE X
MIXTURE I

Temp., °C.	Density	*h* corr.	Surface tension, dynes/cm.	Mol. surface energy, ergs/sq. cm.	Eotvos constant, K_c
0.09	1.0029	3.79	57.13	404.6	
6.20	1.0025	3.66	55.25	391.8	1.6
10.30	1.0021	3.61	54.39	385.5	
20.80	1.0003	3.46	52.14	370.0	
29.70	0 9978	3.19	47.91	340.0	2.2
41.50	.9940	2.92	43.65	326.6	
52.10	.9893	2.81	41.85	299.1	
60.53	.9845	2.63	38.94	279.3	1.1
70.30	.9793	2.52	37.11	267.1	
79.97	.9740	2.38	34.84	252.8	
90.27	.9685	2.30	33.54	243.2	1.3
95.40	.9685	2.22	32.30	234.6	
MIXTURE III					
0.41	1.0192	2.59	48.83	396.3	
7.82	1.0172	2.55	48.12	390.8	
14.85	1.0147	2.51	47.23	384.4	0.8
19.67	1.0129	2.47	46.41	378.5	
25.27	1.0104	2.46	46.06	375.9	
30.46	1.0080	2.43	45.31	370.3	

TABLE X (Concluded)

Temp., °C.	Density	*h* corr.	Surface tension, dynes/cm.	Mol. surface energy, ergs/sq. cm.	Eotvos constant, *Kc*
35.60	1.0056	2.40	44.73	365.5	
44.92	1.0007	2.31	42.88	350.8	1.5
60.00	0.9953	2.14	39.52	325.1	

TABLE XI

MIXTURE IV

Temp., °C.	Density	h corr.	Surface tension, dynes/cm.	Mol. surface energy, ergs/sq. cm.	Eotvos const., *Kc*
0.24	1.0314	2.70	51.55	444.5	
7.70	1.0284	2.64	50.34	435.5	
19.90	1.0223	2.51	47 54	412.7	1.4
24.80	1.0195	2.48	46.73	407.4	
30.56	1.0157	2.43	45.68	399.2	
35.30	1.0130	2.39	44.92	392.1	1.8
46.20	1.0055	2.26	42 13	369.5	
55.86	0.9982	2.17	40.06	353.4	

TABLE XII

MIXTURE V

Temp., °C.	Density	It corr.	Surface tension, dynes/cm.	Mol. surface energy, ergs/sq. cm.	Eotvos constant, I c
1.88	1.0467	2.41	46.77	525.2	
11.17	1.0403	2.43	46.85	527.5	
15.50	1.0370	2.42	46.48	523.7	0.8
19.75	1.0335	2.40	45.99	520.6	
25.62	1.0291	2 36	45.00	508.2	
29.75	1.0257	2.32	44.00	500.9	
34.76	1.0218	2.23	42.13	480.8	
39.55	1.0172	2.19	41.35	473.0	1.9
51.20	1.0070	2.12	39.62	456.4	
61.20	0.9985	2.05	37.96	470.2	

TABLE XIII

MIXTURE VI

Temp., °C.	Density	*h* corr.	Surface tension, dynes/cm.	Mol. surface energy, ergs/sq. cm.	Eotvos constant, Kc
0.42	1.0540	2.43	47.37	622.3	
5.50	1.0500	2.40	46.75	615.2	
10.20	1.0462	2.37	45.88	605.7	1.8
19.85	1.0374	2.31	44.29	587.5	
25.02	1.0327	2.27	43.30	576.8	
29.17	1.0288	2.24	42.65	570.6	1.6
34.97	1.0236	2.20	41.77	560.4	
40.30	1.0185	2.17	40.90	548.8	
50.45	1.0091	2.12	39.67	536.5	
60.00	1.0002	2.08	38.49	523.6	1.4
69.65	0.9914	2.02	37.10	507.6	
75.05	.9862	2.00	36.58	502.3	

The values of the Eötvös constant for nicotine are larger than the theoretical, 2.12. Using the empirical equation of Walden and Swinne,[8] $K_c = 1.90 + 0.011\,(\Sigma NA)$ where (ΣNA) represents the sum of the square roots of the atomic weights of the elements in the compound, a value of K_c is obtained which is numerically equal to 2.50, about the average of the value found experimentally. There appears to be a gradual increase in this value with temperature up to about 75" and then a falling off. Whether this decline would continue until the theoretical value is reached will be discussed in a further communication. In any case there seems to be no basis for considering the nicotine associated. This is further borne out by the consistent values of the Macleod constant and by the values of the Hildebrand[9] functions for nicotine. The values are as follows: $\gamma/V^{1/3} = 7.65$, $E_\sigma/V^{1/3} = 114.1$, in which γ is the surface tension, V the molal volume and E_σ the total surface energy. It is thus seen that nicotine has an internal pressure about equal to that of thiophene and bromobenzene.

If the surface tension values of the solution are plotted against temperature, the curves obtained all show a deviation from a straight line. It would appear from the curves that between 15 and 35° alterations in the nature of the liquid take place which can best be explained by the breaking down of the nicotine hydrates. Likewise, the values of K_c for the different solutions show no regularity of behavior. No higher values are obtained in case of Solution No. 6 with a high nicotine content than with Solution 1, which has the lowest.

It is obviously futile to draw any conclusions as to the state of nicotine and water in the various solutions from a consideration of this change in molecular surface energy with temperature. A much more fertile field of speculation is presented when the surface tensions are plotted against concentrations, as shown in Fig. 2. There we have a series of maxima at about 36.15 and 72.16% which tend to disappear as the temperature rises. Skalweit,[5] as mentioned before, observed a maximum density at a concentration of 72% of nicotine, Tsakalotos[4] a viscosity maximum at 78%, and Jephcott[3] from the specific rotation of nicotine solutions found maxima at roughly 40 and 80% nicotine concentration. Now according to Denison,[10] whenever extensive deviations occur from the straight-line law for mixtures, it is reasonable to assume the existence of a compound at the point of maximum deviation. Also, according to Denison, such deviations as are shown in the figure can scarcely be due to the change in association of either solvent. The most likely explanation of the maxima must then be that they represent the points of maximum concentration of nicotine hydrates which break down as the temperature approaches 60°.

[8] Walden and Swinne, *Z. physik. Chem.*, 82, 290 (1913).

[9] Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, p. 111.

[10] Denison, *Trans. Faraday Soc.*, 8, 20–35 (1911).

Summary

1. The densities and surface tensions of nicotine have been measured from -50 to 94° and of nicotine–water solutions from -50 to 60°.

2. The Eötvös constant for nicotine is shown to be between 2.4 and 2.8 and nicotine does not appear to be associated.

3. Evidence for the existence of nicotine hydrates is shown by the concentration–surface tension curves.

VANCOUVER, B. C., CANADA

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

THE DISSOCIATION PRESSURE OF Fe_4N

BY P. H. EMMETT, S. B. HENDRICKS AND STEPHEN BRUNAUER

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Introduction

In order to learn more concerning the various factors that contribute to the remarkable efficiency of promoted iron catalysts for the production of synthetic ammonia, a number of workers have investigated the conditions under which nitrides of iron can be formed. Baur and Voerman,[1] Maxted[2] and others tried without success to form iron nitride by the action of nitrogen at pressures as high as 200 atmospheres on iron between temperatures of 400 and 700". Noyes and Smith[3] showed the possibility of calculating the exact dissociation pressure of the iron nitrides by combining the equilibrium constants for the reactions

$$N_2 + 3H_2 = 2NH_3 \qquad K_1 = \frac{(P_{NH_3})^2}{(P_{H_2})^3(P_{N_2})} \tag{1}$$

$$2Fe_xN + 3H_2 = 2xFe + 2NH_3 \qquad K_2 = \frac{(P_{NH_3})^2}{(P_{H_2})^3} \tag{2}$$

to obtain K_3 for the reaction

$$2Fe_xN = 2xFe + N_2 \qquad K_3 = P_{N_2} = \frac{K_2}{K_1} \tag{3}$$

At 460° the indirect values thus obtained were found to vary between 20,000 and 500,000 atmospheres, depending upon the nature of the solid phase.

The surface hardening of complex alloy steels by treatment with ammonia at elevated temperatures enhances interest in equilibria for the iron–nitrogen system. Recent x-ray structure investigations by Hägg,[4] by Brill[5] and by Osawa and Iwaizumi[6] of the compounds formed by the action

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[1] Baur and Voerman, *Z. physik. Chem.*, 52, 467 (1905).

[2] Maxted, *J. Soc. Chem. Ind.*, 37, 105 (1918).

[3] Noyes and Smith, THIS JOURNAL, 43, 475 (1921).

[4] Hagg, *Nature*, 121, 826 (1928).

[5] Brill, *Z. Kryst.*, 68, 378 (1928).

[6] Osawa and Iwaizumi, *ibid.*, 69, 26 (1928).

of dry ammonia on iron indicated that Noyes and Smith were probably dealing with mixtures of more than two solid phases and that the compounds actually present in their experiment were Fe_4N, Fe_2N and perhaps Fe_3N, but not in addition, the postulated Fe_8N and Fe_6N. Frankenburger[7] reports that some specimens of iron catalyst when removed from high pressure ammonia converters contain as much as 5% of nitrogen. Accordingly, since the value of the ratio $(P_{NH_3})^2/(P_{H_2})^3$ known to exist in the high pressure ammonia conversions is very much lower than the value found by Noyes and Smith for K_2 at 460°, it is probable either that K_2 changes very rapidly with temperature or else is very much lower than reported. It seemed to be worth while to determine the values of K_2 at several different temperatures, taking care to identify the solid phases by means of their x-ray powder diffraction patterns.

The present paper recounts the determination of the value of the equilibrium constant for the reaction

$$2Fe_4N + 3H_2 = 2NH_3 + 8Fe \quad K_4 = \frac{(P_{NH_3})^2}{(P_{H_2})^3} \tag{4}$$

at 420, 444, 460 and 525°. The dynamic method used consisted in passing various mixtures of ammonia and hydrogen over iron at a fixed temperature and noting the gas composition at which the first nitride formation occurred. The solid phases present at equilibrium were identified by x-ray powder diffraction patterns. From the data obtained the value for the equilibrium constant of the reaction

$$2Fe_4N = N_2 + 8Fe \quad K_5 = P_{N_2} \tag{5}$$

has also been determined.

Apparatus and Experimental Procedure

A flow system apparatus was designed that permitted the passage of a hydrogen–ammonia mixture of definite composition over a sample of iron at a fixed temperature. Tank hydrogen was purified by passage over hot copper and through a phosphorus pentoxide tube. The purified gas analyzed 99.9% of hydrogen in a Bone and Wheeler gas analysis apparatus. The synthetic ammonia used was dried by contact with metallic sodium; it did not contain appreciable free nitrogen or hydrogen. Calibrated flowmeters permitted mixing the two gases in any desired proportion immediately before passing them over the iron sample. The iron used was obtained by the reduction of c. p. ferric oxalate in hydrogen.

The glass reaction vessel as shown in Fig. 1 consisted of reaction chamber A with its inlet and outlet, side tube B, for inserting the charge of ferric oxalate, thermocouple well C, extending through the entire sample and side tube D for taking samples for the x-ray photographs. It was heated by a nichrome wire-wound heating furnace controlled by hand-adjusted rheostats. The variation in temperature never exceeded ±5° during a run. In the experiments carried out at 444° the furnace was replaced by a sulfur bath; the temperature in these runs was constant to within ±0.5°. All tem-

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[7] Frankenburger, Ullmann "Enzyklopadie der Technischen Chemie," p. 393 (footnote), Berlin, 1928.

peratures were determined with a calibrated alumel–chromel thermocouple in conjunction with a Leeds and Northrup portable potentiometer.

The procedure used in each experiment is briefly described below. A weighed charge of ferric oxalate was introduced into the reaction tube and reduced in a stream of hydrogen. After complete reduction of the sample, as determined by absence of water vapor in the exit gases and by x-ray powder photographs, various mixtures of ammonia and hydrogen were passed over it for definite periods of time at a fixed temperature. The composition of the gaseous mixture used was checked at the beginning of each run, both before and after it passed over the iron, by absorbing the ammonia in 4% boric acid and measuring the hydrogen in a gas compensometer. The ammonia absorbed in the boric acid was titrated with standard sulfuric acid using methyl orange as indicator. At a flow of approximately 400 cc. of gas per minute, used in all runs, no cracking was observed on the 1- or 2-g. samples of iron.

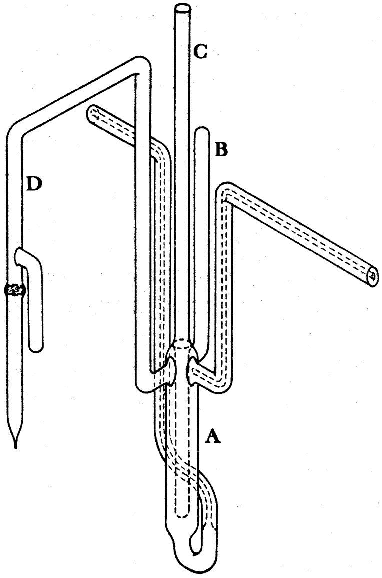

Fig. 1.

Upon completion of an experiment, pure nitrogen was run over the sample for a few seconds to flush out the hydrogen–ammonia mixture; the tube was then quickly cooled in a stream of nitrogen by removing it from the furnace. Finally, an x-ray sample was shaken into the thin-walled side tube D and sealed off. The remaining sample in the reaction vessel was reduced in a current of hydrogen, the temperature being gradually raised from 25 to 525°. The ammonia formed was usually determined as described above; in those runs, however, in which only a small amount of nitride was anticipated, water was used as an absorbent and titrations were carried out with 0.01 *N* sulfuric acid using sodium alizarine sulfonate as indicator.

The x-ray powder diffraction photographs were all taken with iron K radiation obtained from a metal tube operated at 5 to 20 milliamperes and 20,000 to 30,000 volts. An oxide coated filament was used in order to prevent contamination of the anticathode; nevertheless, the anticathode was frequently cleaned. A small cylindrical camera of 3.583-cm. radius was used throughout the work. Sodium chloride and iron were used as reference substances for accurate spacing determinations. With this apparatus a few per cent. of Fe_4N could be detected in an iron sample.

Results

The results of the equilibrium studies are listed in Table I. The fourth column of this table indicates that some nitrogen was present in the sample even when the percentage of ammonia used in the gaseous mixture was not high enough to produce Fe_4N. The nature of this small amount of nitrogen is not well understood. It is possible that part of it is due to ammonia sorbed by the iron and not removed by the thirty-second flushing with nitrogen. Probably, however, most of it is to be accounted for by the formation of a surface nitride, analogous to a previously discussed[8] surface oxide formation occurring when mixtures of steam–hydrogen containing less than the equilibrium percentage of steam are passed over freshly reduced iron, cobalt or nickel. The assumption that this blank is due to a solid solution of nitrogen with iron is improbable, as will be pointed out later.

TABLE I

SUMMARY OF EQUILIBRIUM RUNS

Rate of flow, 400 cc. per min,

Temp., °C.	Time of run, hours	NH_3 in gas mixture, %	N_2 collected, mg.	X-ray diffraction pattern
			Sample **I.**	Weight of iron, **1.19** g.
460	5	25	2.4	Pure Fe, complete absence of Fe_4N
	3	27	2.7	Fe_4N entirely absent
	1	28	1.6	No photograph
	1	29	9.6	No photograph
	3.5	29	52.0	Very strong Fe_4N lines, faint Fe lines
	10	29	55.3	Very strong Fe_4N lines, very faint Fe lines
525	5.5	15	3.5	No photograph
	4	16	4.3	Fe_4N completely absent
	4	17	4.8	Fe_4N completely absent
	3.5	17	7.1	Very faint Fe_4N lines
	2	17.5	10.6	Fe_4N lines present **with** strong Fe lines
	4	17.5	13.5	Fe_4N lines indicating about 25% Fe_4N
	4	19	25.7	About 50–60% Fe_4N
			Sample II.	Weight of iron, **1.78** g.
420	4	**35**	**5.8**	Extremely faint Fe_4N
	4	**36**	**2.8**	Fe_4N completely absent
	4	**37**	**7.0**	Distinct Fe_4N lines
	5	**38**	**23.7**	About **20%** Fe_4N
	5	**39**	**21.1**	About 20% Fe_4N
	5	**40**	**13.8**	Distinct Fe_4N lines
444	4	**29**	**2.1**	Fe_4N completely absent
	4	**30**	**5.7**	Distinct Fe_4N lines present
	3	**31**	**8.7**	Distinct Fe_4N lines present
460	4	**28**	**2.8**	No photograph

Table II shows the equilibrium data deduced from the results listed in Table I. The ammonia percentage in a hydrogen–ammonia mixture

TABLE II

EQUILIBRIUM DATA OF THE REACTION $2Fe_4N + 3H_2 = 8Fe + 2NH_3$

Temp., °C.	% NH_3 in equilibrium	$K = \frac{(NH_3)^2}{(H_2)^3}$
420	**36 ± 1.5**	**0.495 ± 0.08**
444	**30 ± 1**	.262 ± **.03**
460	**28.5 ± 1**	.223 ± .025
525	**17 ± 1**	.051 ± .01

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[8] Emmett and **Shultz,** THIS JOURNAL, 51, **3249 (1929).**

in equilibrium with Fe–Fe_4N at each temperature is given in Col. **2.** The calculated equilibrium constants are listed in Col. **3.**

The results of the x-ray examinations are listed in the fifth column of Table **I.** The only phases present, as indicated by the diffraction photographs, are Fe and Fe_4N. Measurements, using sodium chloride as a reference substance, of the diffraction lines from the iron and the Fe_4N lattices are in agreement with the results obtained by previous investigators, with the exception of Osawa and Iwaizumi. A typical set of x-ray diffraction data from Fe_4N is given in Table III. The average value of a_0 from our measurements for Fe_4N is **3.794** Å. The average value obtained by passing **38%** NH_3 over iron at 420° is 3.79_0 **k.; 29%** NH_3 at 460° is **3.796** Å.; 39% NH_3 at 420° is 3.79_0 Å. The variations noted are within the experimental error.

TABLE III

TYPICAL X-RAY DIFFRACTION DATA FROM Fe_4N. Fe K RADIATION

Intensity	$\Theta/2$	d_{hkl}, Å.	Indices	a_0, Å.
Medium	23° 34'	2.192	111 β	3.797
Very strong	26° 31'	2.189	111	3.791
Medium weak	27° 31'	1.897	200 β	3.794
Medium strong	30° 40'	1.896	200	3.792
Medium weak	40° 53'	1.340	220 β	3.790
Strong	46° 7'	1.341	220	3.793
Medium	50° 2'	1.143	311 β	3.791
Very strong	57° 47'	1.143	311	3.791
Medium	62° 3'	1.095	222	3.793

The diffraction data of Fe_4N can be explained by a cubic lattice containing **1** Fe_4N with the iron atoms at $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$, 000 and the nitrogen atom at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The nitrogen atoms alone contribute to reflections from planes (*hkl*) with one or more indices even in odd orders; such reflections should be relatively very weak. An overexposed x-ray photograph of a sample obtained by passing a **29%** NH_3 gas mixture over iron at 460° and shown by analysis to contain about **90%** Fe_4N, indicated the presence of the reflection from **(100).** The experimental procedure was not sufficiently refined, however, to allow observation of two other reflections, namely, those from **(110)** and (210), reported by Brill.[9]

Samples of the solid phases from one-hour runs at 460° with **31, 30,** and 20% of NH_3, respectively, were mixed with an equal amount of pure iron obtained by reduction of the oxalate. These powder mixtures gave patterns showing no broadening of the diffraction lines. It is estimated that a change in the lattice constant of one part in one thousand could easily be observed by this method. This is in disagreement with the results of Osawa and Iwaizumi,[6] who reported as great as 1% distortion of the edge of the unit cube for alpha iron in a system containing small amounts

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[9] **Brill, *Z. Krist.*, 68, 379 (1928).**

of nitrogen. They suggested that the nitrogen was in solid solution in the iron. Under the conditions of our experiments there is surely no x-ray evidence for the existence of such a solid solution.

It is difficult to calculate accurately the maximum possible error that might exist in any one reading. However, allowing liberally for possible errors in the rates of flow of hydrogen, and of ammonia, and in the temperature of the material in the reaction vessel, we estimate that the greatest deviation at each temperature that could arise even if all of the errors by chance happen to be in the same direction is such as to give for the final percentage ammonia in the equilibrium ammonia–hydrogen mixture the values 36.5 ± 3.3 at 420°, 30 ± 1.5 at 444°, 28.5 ± 2.7 at 460° and 17.0 ± 1.8 at 525°. However, consideration of the number of runs made at each temperature and of the agreement obtained leads us to believe that the equilibrium values at each of the four temperatures can be confined to narrower limits. These limits are, as listed in Table II, 36 ± 1.5 at 420°, 30 ± 1 at 444°, 28.5 ± 1 at 460° and 17 ± 1 at 525°. In Fig. 2 is shown a plot of log K_4 values against $1/T$.

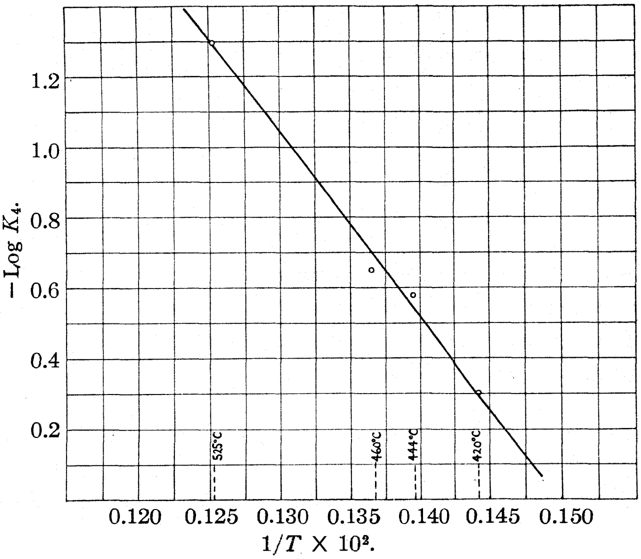

Fig. 2.—Variation of $-\log K_4$ with $1/T$.

Thermodynamic Calculations.—The dissociation pressure of Fe_4N can be calculated, as already described, by combining the known equilibrium constant for Reaction 1 with the present determined constant for Reaction 4. Thus for Reaction 5 the value of $K_5 = P_{N_2} = K_4/K_1$ will vary from 4250 atm. at 420° to 5600 atm. at 525°, as can be seen by reference to Table IV. The values of K_1 are those obtained by the use of the equation given by Haber[10] for one atmosphere equilibrium values for Reaction 1.

$$\log K_1 = \frac{26{,}400}{4.571\ T} - 12.268$$

Due to the lack of any data for the specific heat of Fe_4N, it does not seem desirable to include in the present discussion even approximate values for ΔH_{298}, or ΔF_{298} for Reactions 4 and 5. It may be pointed out, however, that the average value for ΔH for Reaction 4 between 420 and 525° obtained from the slope of the curve in Fig. 2, corresponds to —24,100 calories.

TABLE IV

THE DISSOCIATION PRESSURE OF Fe_4N

Temp., °C.	$K_1 = \frac{(P_{NH_3})^2}{(P_{H_2})^3(P_{N_2})}$	$K_4 = \frac{(P_{NH_3})^2}{(P_{H_2})^3}$	$K_5 = \frac{K_4}{K_1} = P_{N_2}$
420	11.61×10^{-5}	0.495	4250
444	6.12×10^{-5}	.262	4300
460	4.12×10^{-5}	.223	5400
525	0.92×10^{-5}	.051	5600

Discussion

The calculated dissociation pressures obtained in the present paper are entirely consistent with the failure of all direct attempts to synthesize Fe_4N from nitrogen and iron by exposure of the latter to nitrogen at as high pressures as 200 atmospheres, at temperatures between 400 and 700°.

The equilibrium values obtained by us are markedly lower than the value obtained by Noyes and Smith for the systems of low nitrogen content. Thus we found K_4 to be 0.223 at 460°, corresponding to a dissociation pressure of 5400 atmospheres for Fe_4N. Noyes and Smith found K_2 to be unity at 460°, the corresponding dissociation pressure for Fe_xN being 20,000 atmospheres. It seems highly probable that their various Fe_xN samples in which the iron–nitrogen atomic ratios were between 17:1 and 8:1 were mostly Fe_4N and Fe with small amounts of Fe_3N or Fe_2N.

In each of the twenty to thirty minute experiments made in the static system employed by Noyes and Smith, the small amounts of higher nitrides, either because of their probable location on the outer boundary of the Fe_4N–Fe particles, or because of their greater rate of reduction by hydrogen, could rapidly remove a large portion of the hydrogen in the gas mixture and could thereby cause the final value of the ammonia–hydrogen ratio to be too high. Thus the equilibrium values given by Noyes and Smith may be too high, due to the partial or complete establishment of equilibrium between H_2–NH_3–Fe–(Fe_2N or Fe_3N) or H_2–NH_3–Fe_4N–(Fe_2N or Fe_3N) rather than between H_2–NH_3–Fe–Fe_4N as in the present

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[10] **Haber, *Z. Elektrochem.*, 21, 89 (1915).**

work. In any case, the present experimental values can be relied upon to represent within the limits of error already outlined the equilibria of Reactions 4 and 5.

It may be well to point out a few conclusions from the above work that will be of interest to those concerned with the nitrogen content of steels.

The minimum amount of ammonia in a mixture of ammonia and hydrogen that when passed over steel will form a layer of Fe_4N varies from 17% at 525° to 36% at 420°. Intermediate temperatures can be obtained indirectly from the curve of Fig. 2. Contrary to the opinions of many metallurgists,[11] there is no evidence that the liberation of "nascent nitrogen" by ammonia cracking permits ammonia to be more effective as a nitriding agent than pure nitrogen; rather, it may be said that thermodynamically the reverse of Reaction 2 above will occur whenever the ammonia–hydrogen ratio in the mixture above the iron sample exceeds the equilibrium ratio.

The iron–nitrogen "phase rule diagram" as given by various metallurgists[11] and also pictured in the "International Critical Tables"[12] is not in any sense an "equilibrium diagram" if nitrogen at one atmosphere pressure is considered as the gas phase. Such thermal studies as have been made are possible only because of the low rate of decomposition of the nitrides formed.

The increase of the dissociation pressure of Fe_4N with temperature over the temperature range 420 to 525° indicates that alpha iron will not react at any temperature with nitrogen to form Fe_4N. It is at present not clear how the nitride needles reported[13] to be formed by melting iron in nitrogen and quenching suddenly can actually result from the combination of iron and nitrogen. It is possible, however, that gamma iron existing between 920 and 1430' may either possess a different reactivity toward nitrogen or enter into a series of solid solutions with Fe_4N. It is also possible that although the dissociation pressure of Fe_4N and the nature of its change with temperature may preclude the possibility of its being formed by the reaction of nitrogen at one atmosphere pressure with alpha iron, nevertheless, the dissociation pressure of Fe_3N or Fe_2N may change with temperature in such a manner as to make the formation of one of these latter nitrides possible. These systems are now being investigated.

Summary

The equilibrium constants for the reaction $2Fe_4N + 3H_2 = 8Fe + 2NH_3$ have been determined to be 0.495 ± 0.08, 0.262 ± 0.03, 0.223

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[11] Nitriding Symposium, A. S. S. T., XVI, October, 1929.

[12] "International Critical Tables," Vol. II, p. 451.

[13] R. S. Dean, R. O. Day and J. L. Gregg, Technical Publication No. 193, Am. Inst. of Mining and Metallurgical Engineers; C. Baldwin Sawyer, Transactions of A. S. S. T., September, 1925, p. 291.

± 0.025 and 0.051 ± 0.01, at 420, 444, 460 and 525°, respectively. From these constants, together with the equilibrium constants for the N_2–H_2–NH_3 system, the dissociation pressures of Fe_4N according to the reaction $2Fe_4N = 8Fe + N_2$ have been calculated to be 4250, 4300, 5400 and 5600 atmospheres, respectively, at the above temperatures. The solid phases were identified as Fe_4N and Fe by means of x-ray powder photographs. They give no indication of any distortion of the iron lattice as might possibly result if under the condition of our experiments appreciable solution of nitrogen in the iron samples were to occur. The results explain many but not all of the phenomena observed in the nitriding of steels.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 2]

A STUDY OF THE REACTION OF HYDROGEN BROMIDE WITH SILICON

BY WALTER C. SCHUMB AND RALPH C. YOUNG

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Although the facts concerning the reaction of hydrogen bromide upon silicon at elevated temperatures have long been known in a general way, and the similarity of this reaction to that of hydrogen chloride upon silicon has been pointed out, especially by the work of such investigators as Buff and Wöhler,[1] Gattermann,[2] Besson and Fournier,[3] and Combes,[4] no very precise data concerning the necessary conditions, the purity of the materials used, the yields of the various products and the mechanism of this reaction appear to have been laid down; the present investigation was undertaken with the object of throwing further light upon these and allied matters. Inasmuch as a mixture of products is inevitably obtained, and the separation by fractionation of the crude product by the usual methods of distillation is not particularly clean-cut, the boiling points of the bromine derivatives of silane given by the different earlier observers mentioned do not agree closely, so that more recently Stock and his co-workers[5] starting with silane, have prepared these compounds and determined their constants with greater accuracy.

The apparatus used in the present study of the reaction of gaseous hydrogen bromide with crystalline silicon is shown in Fig. 1.

Electrolytic hydrogen was passed through three towers (two of which appear in the figure) containing fused flakes of potassium hydroxide, thence it could be passed directly

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[1] Buff and Wohler, *Ann.*, 104, 99 (1857).

[2] Gattermann, *Ber.*, 22, 193 (1889).

[3] Besson, *Compt. rend.*, 112, 530 (1891); Besson and Fournier, *ibid.*, 151, 1055 (1910).

[4] Combes, *ibid.*, 122, 531 (1896).

[5] Stock and Somiesky, *Ber.*, 50, 1739 (1917).

through the rest of the apparatus in order to sweep out the air, or it could be caused to bubble through liquid bromine at 45° and a mixture of hydrogen and bromine vapor in nearly equimolar proportions thereby obtained. This mixture passed through a pyrex tube containing platinized asbestos which was heated electrically to 200°. The gas passing beyond this catalyst tube showed no color of free bromine, but was nevertheless allowed to pass through a tower containing ferrous bromide, which had been partly dehydrated at 100°, to absorb any traces of the halogen, and finally through two towers (one of which is shown) of freshly fused calcium bromide, before entering the reaction tube containing pulverized commercial silicon (averaging 97.5% Si), which was heated electrically to the desired temperature (usually 360°). The calcium bromide and ferrous bromide towers were frequently refilled. The gaseous products were condensed in a flask deeply immersed in alcohol, which was cooled by addition of solid carbon dioxide to a temperature of about —30"—below this temperature solidification of silicon tetrabromide caused clogging of the tube entering the receiver—and the unchanged hydrogen bromide passing through the remaining portion of the apparatus was vented through a drying tube into the hood.

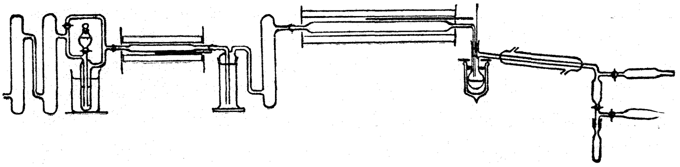

Fig. 1.

The crude product condensed in the flask was twice distilled, the first distillation being directly from the flask, the fractions collected being (a) up to 125° and (b) from 125 to 154". The device indicated in the diagram permitted the evacuation of the receiver, the sealing off of each fraction as collected, and the replacement of a second receiver, which in turn could be evacuated. These precautions were necessary not only because of the danger of hydrolysis of the products, but also because tribromosilane (silicobromoform) is spontaneously inflammable in the air. As a rule, the hydrogen passed at such a rate through the bromine that about 60 g. of the latter was vaporized in a run of five hours, yielding about 57 g. of mixed halides. Variations of this procedure are discussed below.

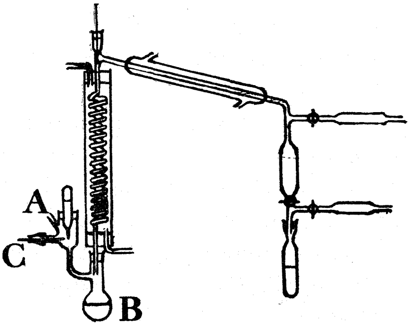

Fig. 2.

The first distillation of the mixture of halides obtained in one series of ten runs gave a fraction, representing about 60% of the total, boiling below 125°, the remainder distilling up to 154°. These proportions, however, were somewhat variable, even when conditions of temperature, rate of flow, fineness of subdivision of the silicon, etc., were kept as nearly constant as possible.

The crude fractions obtained in the first distillation as above described were finally fractionated in the apparatus shown in Fig. 2, the principal features of which were the means of transferring the liquid in an atmosphere of dry nitrogen and the spiral fractionating column, which enabled a remarkably sharp separation of the mixture. This type of column has been found exceptionally satisfactory in the distillation of various mixtures of organic liquids by Professor H. S. Davis,[6] to whom we are indebted for the use of the spiral employed by us. The pyrex spiral was surrounded by a glass air-jacket, through which compressed air, preheated to a few degrees below the boiling point of the fraction being collected, was passed. Variation in the rate of flow of this air through an electrically heated tube enabled rather close adjustment of the temperature of the air-jacket.

In carrying out a fractionation, the sealed tube containing the crude sample was inserted, point downward, into the funnel **(A)**; the whole apparatus was filled with dry, oxygen-free nitrogen; the tip of the sample tube was broken by the glass plunger (C), thus permitting the liquid to run down into the distilling flask (B). By means of this apparatus the crude fractions were separated quite sharply into three, possessing very definite boiling points: 64.0, 111.8, and 153.4" (corrected). These correspond to di-, tri- and tetrabromosilane, respectively. The lowest value, 64.0°, is somewhat lower than that given by Stock and Somiesky (66.0°), but their result was obtained indirectly by a rather long extrapolation of the vapor pressure curve for this substance and may be slightly in error.

The freezing point of silicobromoform is given in the literature as below −60". Our product was found to freeze at −73 ± 1°, and showed a very decided tendency to undercool.

In one series of experiments the quantities of the fractions obtained were as follows: 64°, 7 g. or 2.8%; 111.8°, 166 g. or 66.1%; 153.4°, 78 g. or 31.1%. We were unable to obtain any evidence of the formation of monobromosilane, SiH_3Br, and we feel that if formed it must have been present in only minute quantities. A very small residue of material boiling above 153.4° was left in the distilling flask.

In studying the influence of varying conditions upon the reaction of hydrogen bromide on silicon, it was decided to observe the effect of the following variables: *(a)* the temperature, i. e., to note the lowest temperature at which the formation of reaction products can be detected in a reasonable length of time, and to observe any change in the composition of the products obtained at increasingly elevated temperatures; (b) the rate of flow of the hydrogen bromide gas through the system; (c) the fineness of subdivision of the silicon; (d) the presence of alloying metals with the silicon, such as copper. The results in each case will be briefly indicated.

It was noted that below 340° the speed of reaction becomes so slow as to be imperceptible, but that above this temperature reaction becomes apparent, and at 360° progresses very readily. This is, of course, far below a visible red heat. In most of the work aimed at the preparation of silicobromoform, the temperature was kept close to 360°. To observe the effect of still higher temperatures the reaction tube was heated to 470° and later to 700° (as measured by a Hoskins pyrometer), at which temperature the pyrex tube softened slightly. It was found with rising temperature that the proportion of silicon tetrabromide was increased, and that of silicobromoform was decreased: Thus at 470° the reaction product consisted of approximately 55% $SiBr_4$ and 45% $SiHBr_3$; while

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[6] H. S. Davis, *Ind. Eng. Chem., Anal. Ed.*, *1*, 61 (1929).

at 700° approximately 80% $SiBr_4$ was found, as compared with 31% obtained at 360°.[7]

The rate of flow of the gaseous hydrogen bromide was varied over a wide range, as is shown by the fact that whereas in a normal run 60 g. of bromine was consumed in a five-hour period, in other runs the same quantity of bromine was consumed in periods varying from two and one-half to fifteen hours. Examination of the products formed showed that the variation in the rate of flow of the hydrogen bromide over the range indicated was without noticeable effect upon the nature of the products formed, although a variation was noted in the percentage composition of the products, the fast runs yielding, in general, a greater proportion of silicon tetrabromide than the slowest runs. The significance of this fact will be discussed later.

The particle size of the silicon used was varied from 40-mesh to 150-mesh in successive runs, and in one case an alloy of copper and silicon (90% Cu, 10% Si) was substituted for the silicon; no difference in the nature of the products was detected by these changes. However, it was noted that, using the finely divided silicon, as the quantity of the element in the reaction tube diminished, the proportion of silicon tetrabromide found in the products tended to increase.

As concerns the mechanism of the reaction of gaseous hydrogen bromide on silicon, of several hypotheses which suggest themselves, we believe the following is the most probable. The primary product is silicon tetrabromide, formed by the reaction $Si + 4HBr \longrightarrow SiBr_4 + 2H_2$, and the other compounds are produced either by side reactions, such as $Si + 3HBr \longrightarrow SiHBr_3 + H_2$ and $Si + 2HBr \longrightarrow SiH_2Br_2$, or by consecutive reactions, $SiBr_4 + H_2 \longrightarrow SiHBr_3 + HBr$ and $SiHBr_3 + H_2 \longrightarrow SiH_2Br_2 + HBr$. We are led to this conclusion through consideration of the following experimental facts.

(1) At 360°, hydrogen reduces silicon tetrabromide to a slight extent to silicobromoform. This was observed when a mixture of the vapor of purified silicon tetrabromide (b. p. 153.4°) and hydrogen was passed through a hard glass tube heated to this temperature and the resulting products were condensed; a very small proportion of material boiling below 150°

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[7] This result does not agree with the observations of Gattermann in the study of the reaction of hydrogen chloride with silicon; he found the greater proportion of silicochloroform to be formed at 450–500°, while *lower* temperatures (300–310°) favored the formation of silicon tetrachloride. His silicon had been prepared from silica by reduction with magnesium powder, and its purity was not definitely stated.

In the preparation of silicobromoform, Gattermann used hydrogen bromide prepared from potassium bromide and concentrated sulfuric acid and dried the gas by passage through sulfuric acid, so that his gas must have contained free bromine, as well as sulfur dioxide; furthermore, his reaction product was colored reddish and doubtless contained free bromine. It is not surprising, therefore, to note that Gattermann found the product to consist mainly of silicon tetrabromide, with a small percentage of silicobromoform.

was obtained on distillation of this condensate. When the experiment was repeated at 600°, a similar result was obtained, and when another trial was made at 600°, the heated tube now being filled with powdered silicon, the products, when fractionated with a small spiral column of the type above described, yielded a small quantity of silicobromoform, (b. p. 111.8°).[8]

(2) Silicobromoform is not converted, at 360°, into silicon tetrabromide by hydrogen bromide. When a mixture of gaseous hydrogen bromide and the vapor of silicobromoform was passed through a glass tube heated to 360°, no evidence of material boiling above 111–112° was obtained.

(3) It is improbable that dibromosilane reacts with hydrogen bromide to form silicobromoform, inasmuch as the di-halogen substitution products of methane, CH_2Br_2, and of monogermane, GeH_2Br_2, are known not to react with hydrogen bromide.[9] When this is considered in conjunction with the preceding fact, (2), it may be concluded that silicon tetrabromide cannot be formed from the less highly brominated compounds by the action of hydrogen bromide, but must rather be a primary product of the reaction.

(4) At higher temperatures, as at 700°, silicobromoform is decomposed almost completely into silicon tetrabromide, silicon and hydrogen (together with a very small proportion of hydrogen bromide). In our experiments the proportions of products obtained indicate that the decomposition progresses almost entirely according to the equation $4SiHBr_3 \longrightarrow 3SiBr_4 + Si + 2H_2$. This fact accounts for the decreasing yield of silicobromoform and increasing proportions of the tetrabromide noted above in the reaction of hydrogen bromide on silicon at elevated temperatures.

Summary

The reaction of gaseous hydrogen bromide with pulverized crystalline silicon has been studied with the object of determining the effect of varying conditions upon the nature and the percentage composition of the products. It was found that reaction becomes perceptible at about 340°, and progresses readily at 360°. The proportion of silicon tetrabromide formed increases with rising temperature, while that of silicobromoform decreases. Increase in the rate of flow of hydrogen bromide and decrease in the quantity of silicon in the reaction tube likewise favor increasing proportions of silicon tetrabromide formed. A small proportion of dibromosilane was obtained at the lowest temperatures, but monobromosilane, if formed, must be present in only very minute quantity.

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[8] In this connection Friedel and Ladenburg [Bull. *soc. chim.*, [2] 12, 92 (1869)] noted that when a mixture of silicon tetrachloride and hydrogen is heated to redness, a little silicochloroform is produced.

[9] Compare, for example, Dennis and Judy, THIS JOURNAL, **51**, 2321 (1929).

It is pointed out that at 700° silicobromoform is almost wholly decomposed into silicon tetrabromide, silicon and hydrogen.

The corrected boiling points of the products were: $SiBr_4$, 153.4°; $SiHBr_3$, 111.8°; SiH_2Br_2, 64.0°. The freezing point of silicobromoform was fixed at $-73 \pm 1°$.

As concerns the mechanism of the reaction, it is believed that the primary products are silicon tetrabromide and hydrogen and that the former is reduced in part by the hydrogen to form the other products. Experimental evidence in favor of this hypothesis is given.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NORTH CAROLINA]

A STUDY OF THE QUANTITATIVE PRECIPITATION OF CALCIUM OXALATE IN THE PRESENCE OF THE PHOSPHATE ION

BY J. T. DOBBINS AND W. M. MEBANE

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In the course of the analytical work involved in a previous problem,[1] the authors found it necessary to make calcium determinations on a large number of solutions containing an excess of phosphoric acid. To avoid the long and tedious process of removing the phosphate ion as the ferric salt, a short method was devised whereby the calcium oxalate precipitation was made in the presence of the phosphate ion. Consistent results were obtained by the method, and on the completion of the previous problem a study was made to determine the general applicability of the method.

The method is based on the assumption that the so-called tertiary calcium phosphate, which forms on the addition of ammonium hydroxide to the solution, having a much greater solubility product than calcium oxalate, would go into solution and the calcium oxalate form. Consequently, if the solution be allowed to stand long enough for this metathesis to be complete, it would be possible to precipitate calcium oxalate in the presence of the phosphate ion. In order to determine the most favorable conditions under which to carry out the precipitation, several series of analyses were made to determine the time required for a complete transformation of calcium phosphate into calcium oxalate and the effect of temperature and alkalinity of solution at time of precipitation.

After first having found the minimum time necessary for the complete precipitation, series of analyses were made to determine the difference in results, if any, caused by adding the precipitating agent before and after the solutions were made alkaline with ammonium hydroxide. These series were run both at 20 and at 100°. Some preliminary experiments indicated

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[1] Mebane, Dobbins and Cameron, *J. Phys. Chem.*, 33, 961 (1929).

that an excessive amount of the ammonium hydroxide, when added first to the solution, hindered the formation of the calcium oxalate. Consequently two series were made using a slight excess of ammonia in one case and a 10-cc. excess of concentrated ammonium hydroxide solution in the other, in order to determine the effect of the concentration of ammonium hydroxide on the solution.

Procedure

A 0.1 N solution of calcium chloride was prepared by dissolving a weighed quantity of Iceland spar in hydrochloric acid. Approximately 0.1 N solutions of disodium phosphate and potassium permanganate were made. As the precipitating agent, a saturated solution of ammonium oxalate was used.

Twenty cc. of the standard solution was taken for each analysis. To this solution 25 cc. of the disodium phosphate was added to give an excess of phosphate ions, then an excess of ammonium oxalate. The precipitates were filtered, washed by decantation with distilled water containing a small amount of ammonium hydroxide and transferred on the filter paper to the precipitation beaker. The precipitates were dissolved in dilute sulfuric acid, the solution was brought almost to boiling temperature and titrated with the 0.1 N permanganate solution. It was found that unless the titration required an unusually long time for completion, the presence of the filter paper in the titration beaker did not affect the results. It was found that as accurate results were obtained by titrating the precipitate first formed as by following the usual procedure of dissolving and reprecipitating the calcium oxalate. The losses involved in redissolving the precipitate are as great as the error caused by the adsorption of ammonium oxalate by the precipitate. In all cases the precipitation was carried out in a volume of 80–90 cc.

Data

EFFECT OF TIME OF STANDING. 20 CC. $N/10$ CALCIUM SOLUTION USED IN ALL CASES

	Made alkaline with ammonia before addition of oxalate		Made alkaline with ammonia after addition of oxalate	
Time, hours	20° $N/10$ $KMnO_4$, cc.	100° $N/10$ $KMnO_4$, cc.	20° $N/10$ $KMnO_4$, cc.	100° $N/10$ $KMnO_4$, cc.
0.25	15.40	19.80	20.30	19.80
0.5	20.80	20.05	20.62	19.75
1	20.01	19.95	20.05	19.95
1.5	19.96	20.00	20.00	20.00
2	20.00	20.00	20.05	19.96

EFFECT OF TEMPERATURE, CONCENTRATION OF AMMONIA AND ORDER OF ADDING REAGENTS

Ammonium hydroxide added to the solution before ammonium oxalate. One hour allowed for reaction

20°C.		100°C.	
Slight excess NH_4OH $KMnO_4$, cc.	10 cc. excess NH_4OH $KMnO_4$, cc.	*Slight* excess NH_4OH $KMnO_4$, cc.	10 cc. excess NH_4OH $KMnO_4$, cc.
19.94	20.10	20.00	20.01
20.06	20.06	20.00	20.15
20.11	19.96	20.00	20.08
20.05	20.10	20.11	20.06
20.10	19.95	19.96	20.10

24 hours allowed for reaction

20 °C.		100 °C.	
Slight *excess* NH_4OH $KMnO_4$, *cc.*	10 *cc. excess* NH_4OH $KMnO_4$, *cc.*	Slight *excess* NH_4OH $KMnO_4$, *cc.*	*10 cc. excess* NH_4OH $KMnO_4$, cc.
20.06	20.06	20.00	20.00
20.00	20.06	19.94	19.94
19.94	19.96	19.96	19.80
Ammonium hydroxide added to the solution after ammonium oxalate. One hour allowed for reaction			
20.06	19.66	19.90	19.80
20.00	19.71	19.91	19.94
20.00	19.66	19.76	19.74
20.00	19.91	19.89	19.89
19.80	20.06	19.94	19.96
24 hours allowed for reaction			
20.00	20.11	20.00	20.11
20.00	20 11	19.94	20.06
20.06	20.00	20.06	19.94

Discussion

In some respects the results of these analyses were contrary to our expectations. It was thought that more time would be required for the transformation of the precipitate than is required for the usual precipitation, at least in the case where a considerable precipitate of calcium phosphate was formed before the addition of ammonium oxalate. In many cases good results were obtained when the precipitate stood for only thirty minutes, though this time seems to be too short for consistent results.

The formation of the calcium phosphate precipitates before the addition of the ammonium oxalate not only did not hinder the reaction, but seemed to be a help. These oxalate precipitates seemed to hold the flocculent nature of the phosphate which they replaced, and therefore were very easy to filter and wash. Those to which the oxalate was added first were very fine grained and difficult to filter under the best conditions. In both cases filtration was difficult when the precipitation was carried out at boiling temperature. The agitation during the boiling seemed to deflocculate the precipitate and leave a very fine grained precipitate which had a tendency to run through the filter paper and was very difficult to wash. Although some difficulty was met at first in getting good results with the addition of the ammonia before the oxalate, it was later found that better and more consistent results could be obtained by this method. The addition of the oxalate first gives accurate results, provided the solution is allowed more time in which to precipitate, but the results are likely to be low if the precipitation is carried out at boiling temperature. This may be due to the extreme fineness of the precipitate and the consequent difficulty of removing it completely from the solution.

Recommended Procedure.—Accurate results were obtained from the following procedure: the solution was made alkaline with ammonium hydroxide and 6-cc. excess of concentrated ammonium hydroxide added. An excess of ammonium oxalate was then added at room temperature, stirred and the precipitate allowed to stand for at least one hour. The precipitate was filtered off, washed with water containing a small amount of ammonium hydroxide, transferred on the paper to the precipitation beaker, dissolved in dilute sulfuric acid and titrated with a 0.1 *N* potassium permanganate solution. Considerable variation from this scheme may be made with the results obtained within the normal range of error, but the above outline was found by a large number of analyses to be the most dependable.

Summary

1. Calcium oxalate may be precipitated quantitatively in the presence of phosphate ions.
2. The solutions should be made alkaline before the addition of ammonium oxalate, and a small excess of ammonium hydroxide added.
3. The best temperature for precipitation is 20–25°.
4. Reprecipitation of calcium oxalate is not always necessary.

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

THE DECOMPOSITION OF NITROGEN PENTOXIDE IN INERT SOLVENTS

BY HENRY EYRING AND FARRINGTON DANIELS

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The nitrogen pentoxide decomposition has been used to test theories of reaction rates—the radiation hypothesis, the collision theory and the chain mechanism. The theory of activation through collision is promising but more experimental facts are needed. It is necessary to distinguish between activation caused by ordinary collisions and activation caused by collisions with the decomposition products.

The mechanism of activation does not affect the decomposition rate provided that the rate of activation is high enough to maintain the equilibrium number of activated molecules. A decision may be made between the collision theory and the chain theory by providing conditions which will deactivate the products of decomposition before they collide with unactivated nitrogen pentoxide molecules. Several investigators have sought to make collisions of the decomposition products with the walls relatively numerous as compared with collisions with nitrogen pentoxide. Sprenger[1]

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

reported that the decomposition rate fell off markedly at low pressures, but Tolman[2] found the decomposition rate down to 0.2 mm. to be the same as the normal rate at high pressures.[3,3a]

The present investigation is concerned with the rate of decomposition of nitrogen pentoxide in various inert solvents. The decomposition in chemically active solvents is reported in the following communication. In solution the decomposition products must collide many times with solvent molecules before encountering a nitrogen pentoxide molecule and it is possible that a chain mechanism, if it exists, might be hindered under these conditions.

In this Laboratory it was found by Lueck[4] that the decomposition rate of nitrogen pentoxide is only slightly affected by inert solvents but new developments in the field of kinetics have made it necessary to extend the work to more solvents with the greatest possible precision. The slight deviation from the normal decomposition rate caused by solvents becomes a matter of considerable interest.

The study of nitrogen pentoxide decomposition in solutions makes it possible to bridge the gap between unimolecular reactions in the gas phase and in the liquid phase. The choice of inert solvents is restricted but some exhibit catalytic effects sufficient to double the decomposition rate. In solution it was possible to study solutions up to a calculated osmotic pressure of seventy-five atmospheres—a concentration which cannot be reached in the gas phase. The results are of value in the study of concentrated solutions, and measurements on saturated solutions are of interest in connection with the concept of activities as applied to reaction rates.

Preliminary Experiments

Mr. Roger H. Lueck[4] reported the decompostion rate of nitrogen pentoxide in carbon tetrachloride and chloroform, and then extended the measurements to other solvents. His later measurements also gave excellent unimolecular constants and the decomposition rates at 35° in the different solvents were as follows: CS_2 (fastest), $CH_3(C_2H_5)CHBr$, $CHCl_3$, CCl_4·$C_2H_2Cl_4$, vacuum (*i. e.*, gas phase), CH_3NO_2 (slowest). These results[5] were not published because a satisfactory interpretation was not available and because it was feared that some secondary phenomenon might be involved. The more extensive measurements of the present investigation have con-

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[2] Ramsperger, Nordberg and Tolman, *Proc. Nat. Acad. Sci.*, 15,450 (1929).

[3] Daniels and Johnston, THIS JOURNAL, 43, 53 (1921).

[3a] Recent investigations indicate that the specific decomposition rate falls off at pressures below 0.05 mm., Ramsperger and Tolman, *Proc. Nat. Acad.*, 16, 6 (1930); Schumacher and Sprenger, *ibid.*, 16, 129 (1930).

[4] Lueck, *ibid.*, 44, 757 (1922).

[5] Quoted in *Trans. Faraday Soc.*, 24,732 (1928); and "L'Activation et la Structure des Molécules," Paris, 1928.

firmed the general order of solvents observed before and show that the earlier results were subject to small fluctuations caused by an unpredictable concentration effect which affected the calculation of the activation energy. Carbon disulfide and isopropyl bromide were found to undergo chemical reaction.

Experimental Procedure

Apparatus.—The apparatus was similar to that described before by Lueck[4] but it was decided to eliminate any chance of water leakage or of chemical contamination by using an all-glass apparatus.

The apparatus is shown in Fig. 1. A small flask of 5-cc. capacity containing the nitrogen pentoxide in solution was connected to the gas buret through a coil of thin-walled glass tubing 1 mm. in diameter and about 1 meter long. The glass tube had sufficient flexibility to permit rapid shaking of the solution in a pendulum cradle. The flask contained two or three glass pearls to assist in agitating the liquid. The solution was introduced through the side arm, which was then sealed off. The flask was then placed in the thermostat and strapped to the shaker.

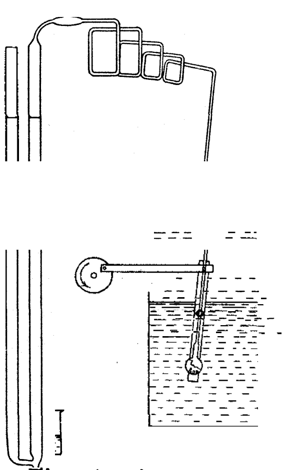

Fig. 1.—Apparatus for measuring the decomposition rate of nitrogen pentoxide in solution by the evolution of oxygen.

The buret was filled with nitrobenzene, which was drained out as needed to maintain the level in the two arms. Before reaching the buret the oxygen passed through glass wool saturated with concentrated sulfuric acid to remove any nitrogen dioxide. The flask was made small to economize nitrogen pentoxide and to minimize any error due to the partial pressure of nitrogen dioxide produced by the decomposition.

Temperature.—A thermoregulator with oscillating contact kept the temperature of the thermostat within 0.01°. The temperature was determined by reference to a thermometer from the U. S. Bureau of Standards.

The shaker operated through an arc of 10 cm. 360 times per minute and it was shown by experiments that this agitation was ample to prevent supersaturation of the solution with oxygen.

A thermocouple inserted in the solution showed that at 600 oscillations the temperature of carbon tetrachloride in the flask at 45° was raised 0.0277° by the mechanical shaking but at 360 oscillations it was raised less than 0.02". The thermocouple gave a zero reading when the shaker was stopped. This temperature rise makes a difference of less than 1% in the reaction rate and is within the limit of experimental error.

The heating was slightly less when the nitrogen pentoxide was decomposing, due probably to the evaporation of the solvent by the escaping oxygen gas. The experiment shows that the shaking is not a source of error and is particularly gratifying in proving also that the reaction is carried out under isothermal conditions in spite of any heat changes from the reaction.

Materials.—The nitrogen pentoxide was prepared by the method of Daniels and Bright.[6]

Solvents of different purity were used but no difference in the results could be detected. For most of the experiment very pure liquids were used—prepared by Pro-

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[6] Daniels and Bright, THIS JOURNAL, 43, 53 (1921).

fessor Timmermans in Brussels under the authority of the Bureau International d'Étalons Physico-Chimiques and distributed by the United States Bureau of Standards. The constants of these very pure compounds have been published by Professor Timmermans.[7]

The liquid nitrogen tetroxide was made by heating lead nitrate. It was then stored in a sealed tube with phosphorus pentoxide and distilled into the flask as needed.

The flask was filled in different ways. Sometimes the crystals were sublimed into the flask and the solvent mas added later and sealed off. Sometimes the nitrogen pentoxide was dissolved in a large reservoir, kept cold and pipetted into the flask. No systematic difference could be detected in the results. The solutions were usually of a light straw color at 0°, indicating a trace of nitrogen dioxide from the decomposition. When placed in the thermostat at 45° the solution turned brown very quickly on account of the decomposition.

Dry Solutions.—In several experiments special precautions were taken to exclude moisture. The nitrogen pentoxide and solvent were distilled into U-tubes containing phosphorus pentoxide, the arms were then sealed off and the tubes stored overnight in contact with the phosphorus pentoxide at 0°. The materials were then distilled into the reaction flask, which was sealed off while immersed in liquid air. A vacuum was applied through the tube and gas buret to facilitate the distillation. The apparatus was thoroughly heated and evacuated before each experiment.

Saturated Solutions.—The decomposition rate in saturated solutions is a matter of particular interest. The thermostat was set at 15° in these experiments because the solubility is too great at higher temperatures, and inconveniently large quantities of oxygen are evolved.

An excess of nitrogen pentoxide was sublimed into the flask, a weighed quantity of the solvent was introduced at 0° and the arm was sealed off. As soon as some nitrogen pentoxide in solution decomposed, its place was immediately taken by more nitrogen pentoxide from the crystals and in this way the concentration in solution was maintained ~~constant. An excess of crystals was present at all~~ times. The solubility was determined by heating the solution (freed from crystals) and measuring the total evolution of oxygen.

Experimental Results

Calculations.—The specific reaction rate k is given by the equation used before[4]

$$k = \frac{2.303}{t_2 - t_1} \log \frac{V_\infty - V_1}{V_\infty - V_2}$$

in which V_1 is the volume of oxygen liberated at time t_1, V_2 is the volume at time t_2, and V_∞ is the final or total volume.

The critical increment E is calculated with the help of the familiar equation

$$\log \frac{k_2}{k_1} = \frac{E\ (T_2 - T_1)}{2.303\, RT_2T_1}$$

in which R is the gas constant and T is the absolute temperature.

Usually six to ten constants were calculated at intervals over the course of the reaction. The average was checked with logarithmic graphs. The constants were uniform and the average deviation was usually less than 3%. The data showed no trend except that over the range of the last *cc.* there was

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[7] Timmermans and Martin, *J. chim. phys.*, **23**, 733 (1926); **25**, 251 (1928).

a tendency for the constant to increase slightly, due in many cases to the magnification of errors in this region. In the most concentrated solutions the constant was higher by about 8% at the beginning of the reaction and a calculation indicated that the volatilization of nitrogen pentoxide during the first part of the experiment could cause the constant to be greater by about 8% at the beginning.

Solvent Effect.--The data for different solvents are given in Table I. In these experiments the concentration was kept nearly the same, approximately one-thousandth of a mole in 5 cc. of solution, corresponding to a calculated osmotic pressure of about 5 atmospheres.

TABLE I

SPECIFIC DECOMPOSITION RATE OF NITROGEN PENTOXIDE IN DIFFERENT SOLVENTS

Values of k × 10^4

Solvent	15°	20°	25°	35°	40°	45°	E
Nitrogen tetroxide	0 159	0 344	. .	. .	. .	. .	25,000
Ethylidene chloride		322		2 54	(4 22)	(7.26)	24,900
Chloroform		274	0.554	. . .	(3.78)	(7.05)	24,600
Ethylene chloride		238	.479	. .	(3 70)	(6 21)	24,400
Carbon tetrachloride		.235	469	. .	(3.62)	(6.29)	24,200
Pentachloro-ethane		.220	.430	. .	(3.26)	(6.02)	25,000
Bromine	114	215			. .	. .	24,000
Gas phase[a]	.079	.165		. . .	2.52	4.73	24,700
Nitromethane	.0747	. . .		. .	(2.14)	4.33	24,500

[a] Calculated from data of Daniels and Johnston, THIS JOURNAL, 43, 53 (1921).

Over a hundred and fifty determinations were made and practically all of them gave satisfactory unimolecular constants. It was not realized for a long time, however, that the magnitude of the constants depended on the concentration of nitrogen oxides, and although this concentration effect was small, it was sufficient to lead to considerable errors in the calculation of the critical increment, E. Although several experiments were averaged, the value of E varied by two or three thousand calories.

It was necessary to adopt a new technique in which the value of k was determined at two temperatures using the same solution. Better results were obtained at lower temperatures with lower reaction rates. The solution was put into the thermostat at 20° and the rate of gas evolution determined. Before the decomposition was half finished, the apparatus was removed to a thermostat at 25° (or other temperature) where the rate of gas evolution was determined, and the final volume, V,, measured. The final volume was then calculated for the lower temperature, and values of k were calculated at both temperatures.

These last results are all recorded in the columns of Table I under 15, 20 and 25° (and 45° for nitromethane). They are used in calculating the critical increments, E, given in the last column. All the values of E are probably the same within the limit of experimental error.

The values of k at 40 and 45°, given in parentheses, represent the averages of several experiments obtained with the first technique in which different solutions were used at the two temperatures. It is to be noticed that the order of solvents is practically the same in all cases. The solvent effect is very real and reproducible. The values in parentheses cannot be used, however, for calculating the critical increment because the concentration at the two temperatures was not always the same. In some cases the concentrations happened to be the same and then the value of E is the same as the more reliable value calculated from data obtained with the new method and recorded in the last column.

Concentration Effect.—It was noticed that the specific decomposition rate k was faster at the higher concentrations. Accordingly, a stock solution of nitrogen pentoxide in carbon tetrachloride was kept at a low temperature and a series of experiments was carried out after diluting with definite quantities of carbon tetrachloride. The results are recorded in Table II.

TABLE II

INFLUENCE OF CONCENTRATION ON DECOMPOSITION RATE OF NITROGEN PENTOXIDE IN CARBON TETRACHLORIDE AT 45°

1. 5.33 moles N_2O_5/liter			2. 2.33 moles/liter			3. 1.40 moles/liter		
Time	Cc. of O_2 remaining	$k \times 10^4$	Time	Cc. of O_2 remaining	$k \times 10^4$	Time	Cc. of O_2 remaining	$k \times 10^4$
0	32.60	. .	0	9.58		0	5.93	. .
82	30.79	6.97	184	8.53	6.32	423	4.61	5.95
162	29.19	6.67	319	7.84	6.23	753	3.75	6.26
409	24.82	6.57	526	6.89	6.22	1116	3.04	5.78
604	20.57	6.37	867	5.57	6.23	1582	2.30	5.98
1129	14.49	6.67	1198	4.56	6.03	1986	1.83	5.66
1721	9.60	6.95	1877	2.98	6.27	2343	1.47	6.13
1929	8.30	6.99	2315	2.25	6.42	. .	. .	. .
3399	3.27	6.69	3144	1.38	5.88	. .	. .	. .

It is obvious that the decomposition in the concentrated solution (1) is fastest and that it decreases in speed as the solution is diluted. The effect is rather unexpected in view of the unimolecular character of the decomposition. For example, in the latter part of Expt. 1 the concentration of nitrogen pentoxide is the same as at the beginning in Expt. 3, but the rate is faster in No. 1 and still there is no deviation from the unimolecular law. Apparently there is a concentration effect in which the decomposition products N_2O_4 and NO_2 are just as effective as the original nitrogen pentoxide molecules. In a single experiment the nitrogen pentoxide in solution (0.1 mole fraction) becomes less and approaches zero while the nitrogen tetroxide starts at nearly zero and increases until it has nearly the same concentration as the original nitrogen pentoxide. Further experiments at 45° on the concentration effect are shown in Fig. 2. The unimolecular constant k is plotted against the concentration of nitrogen pentoxide expressed in moles per liter. In the most concentrated solutions the loss of nitrogen pentoxide through volatilization with the oxygen could cause the constant k to increase by as much as 8% at the beginning of the reaction, and the averaged value over the whole course of the reaction would be somewhat too high. The observed concentration effects are much greater than this.

In this connection it is interesting to note that in the earlier work it was observed that determinations in nitromethane checked better than those in carbon tetrachloride. This fact may be explained by the smaller concentration effect in nitromethane.

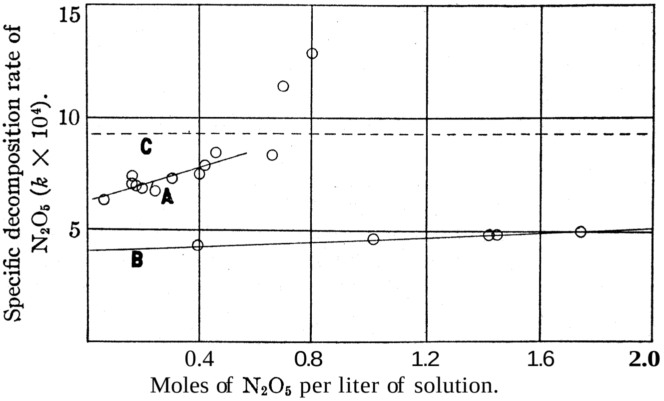

Fig. 2.—Influence of concentration on the specific decomposition rate of nitrogen pentoxide in solution at 45°: A, carbon tetrachloride; B, nitromethane; C, nitrogen tetroxide.

Moisture.—The experiments using special precautions to make the solutions as dry as possible may be summarized as follows. In one case k was found to be 5.83 X 10^{-4} and in another it was 5.68, giving an average of 5.75×10^{-4}. The average of several experiments without special drying precautions was 6.29. The difference between 5.75 and 6.29 might be attributable to the concentration effect. In another experiment 0.04 g. of water was added directly to the solution but the value of k was not affected. No change was observed in the decomposition rate in nitromethane when the solution was dried in the manner described for carbon tetrachloride. If moisture has any effect at all on the decomposition rate, it is a very small effect.

Saturated Solutions.—The specific decomposition rates, k, in saturated solutions are given in Table III. The values of k are calculated from the formula

$$k = -1/c \, dc/dt$$

where c is the solubility (in volume of oxygen) and dc/dt is the constant rate of evolution of oxygen.

TABLE III

DECOMPOSITION RATE IN SATURATED SOLUTIONS AT 15°

Solvent. .	CCl_4	CH_3NO_2
O_2 per 2 cc solvent (per sec), cc	0 0022	0 00148
Soly of N_2O_5 per 2 cc solv , as cc of O_2	120	110
$k \times 10^4$	0 183	0 135

The value of k in each case is much higher than in dilute solutions, a fact which is in accord with the concentration effect noted before. The value of k for N_2O_5 almost saturating N_2O_4 is 0.159×10^{-4}.

Mixed Solvents.—In order to test the influence of polar molecules o-dinitrobenzene and *m*-dinitrobenzene were dissolved in carbon tetrachloride and the solution was used as the solvent for nitrogen pentoxide.

Although the dielectric constants are different, the decomposition rates in these solutions are practically the same as in pure carbon tetrachloride, as shown in Table IV. Nitrogen pentoxide does not react with dinitrobenzene.

TABLE IV

DECOMPOSITION OF NITROGEN PENTOXIDE IN CARBON TETRACHLORIDE SOLUTIONS OF DINITROBENZENE AT 45°

1.	Carbon tetrachloride	0 000619
2.	0 2 M *o*-dinitrobenzene in carbon tetrachloride	.000582
3.	0 2 M m-dinitrobenzene in carbon tetrachloride	000586

A determination was made in a mixture of nitromethane and carbon tetrachloride. In a mixture of 0.1 mole fraction of nitromethane and 0.9 mole fraction of carbon tetrachloride, the value of k was found to be 5.51×10^{-4}. The effect of these solvents appears to be proportional to their mole fraction and independent of catalytic effects produced by small quantities of the solvent.

Theoretical Discussion

All the experiments give confidence that the decomposition of nitrogen pentoxide in these solutions is a simple unimolecular reaction which is significant for theoretical study. The reproducibility of results, the unfailing unimolecularity of the calculated rates, the small differences in velocity caused by a change in concentration (from 0.1 to 1.8 molar) or in solvent preclude the possibility that the reaction is complicated by traces of catalysts. Some bimolecular reactions follow the unimolecular equation simply because the solvent is in large excess, but these experiments were extended to include concentrated solutions up to 1.8 molar or approximately $^1/_3$ mole fraction.

In a second communication which follows this one it will be shown that an intermediate reaction may occur without destroying the unimolecularity of the constant, but gas analysis of the products and refractive index measurements failed to show any reaction with the solvents described here.

The relative influence of the different solvents on the decomposition rate has been checked so many times and under so many different conditions that the solvent effect must be a significant thing, depending on the nature of the solvent rather than on secondary phenomena such as dissolving of water from the air or the presence of catalysts.

The Arrhenius Equation.—The mechanism of the reaction can be studied best after expressing the facts mathematically and for this purpose the Arrhenius equation is very satisfactory, as given in the following forms

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{E}{RT^2} \tag{1}$$

$$\log k = \frac{-E}{2.303\,R} \times \frac{1}{T} + \log s \tag{2}$$

$$k = s\,e^{-E/RT} \tag{3}$$

$$\log k_2/k_1 = \frac{E\,(T_2 - T_1)}{2.303\,RT_2T_1} \tag{4}$$

in which k is specific reaction rate, *i. e.*, fraction of molecules decomposing per second; E is critical energy of activation, or the excess which one mole must have in order to decompose; R is gas constant; T is absolute temperature; s is constant. For the decomposition of nitrogen pentoxide in the gas phase[3] the equation becomes

$$k = 5.08 \times 10^{13}\, e^{-24{,}700/1.98\,T} \tag{5}$$

and at 298°K.

$$k = 0.0000338 = 5.08 \times 10^{13}\, e^{-24{,}700/1.98 \times 298} \tag{6}$$

$$\log k_{308}/k_{298} = \log \frac{0.000131}{0.0000338} = \log 3.88 = 0.5888 = \frac{24{,}700\,(308 - 298)}{2.303 \times 1.98 \times 298 \times 308} \tag{7}$$

The constant s has the dimensions of a number divided by time, and Dushman[8] and others have pointed out that it may have the physical significance of a frequency of light. Polanyi and Wigner[9] have given a derivation recently showing that it is a frequency and that the time depends on the surging of energy among the atoms in a molecule after activation.

As a first approximation, the present authors will take the simple view that s is a frequency and that $1/s$ or, better, $^1/_2\,s$ represents the time taken for the two atoms or groups of atoms at a valence bond to fly apart, after activation—*i. e.*, the natural vibration period in the valence bond which is to break. Certainly it is dimensionally correct and of the right magnitude to correspond to atom vibrations in the molecule—*i. e.*, in the short infrared. Fortunately, in the infra-red region of the spectrum the frequency of light absorbed by the molecule is nearly the same as the frequency of oscillation of its parts. It is possible then to estimate the order of magnitude of s from known infra-red absorption spectra. The significance of s will be discussed more fully in a later communication.

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[8] Dushman, This Journal, **43,** 431 (1921).

[9] Polanyi and Wigner, *Z. physik. Chem.*, **139A,** 439 (1929).

In the study of unimolecular reactions ten years ago it was thought that a molecule decomposed instantly as soon as it was activated, and it was difficult to explain the reaction on the basis of collisions. This difficulty led to the invention of the ill-fated radiation hypothesis. It is evident now that decomposition is not synonymous with activation and that the atoms held together at a valence bond cannot fly apart in less time than the natural period of vibration of those atoms. Molecules receive energy of activation, E, from collisions but it is distributed in a random manner among the atoms and time is necessary before this energy is localized in the particular valence bond. During the rearrangement period many of the activated molecules are deactivated by collisions, and since the number decomposing depends on the equilibrium number in this specially activated condition rather than on the total number activated, the reaction appears to be independent of the number of collisions; *i. e.*, the reaction follows the unimolecular equation.

If the Arrhenius equation is correct (and it is in excellent agreement with the facts), and if the constant s corresponds to the frequency of atom vibrations in the molecule, several relations may be deduced which were formerly regarded as empirical facts. In this discussion the following numerical relations will be helpful.

According to Equation 7 an error of 2% in k_1 makes an error of 1.4% in E or 350 calories, whereas in Equation 6 it makes an error of only 0.05% or 12 calories. k is increased a thousand times by decreasing E 16% or 4000 calories according to Equation 6 but a 16% decrease in E produces only a 16% decrease in log k_2/k_1 according to Equation 7 and k_{308}/k_{298} is changed only from 3.88 to 3.12. From Equation 6 it is seen that the value of k can be doubled by decreasing E only 425 calories, or 1.7%.

Most reaction rates which are measurable at room temperature double or treble for a ten degree rise. Experimental measurement of reaction velocities has been ordinarily limited to a thousand or ten thousand-fold range because it is difficult to measure very rapid reactions on account of the uncertain time of mixing or of bringing the system to temperature equilibrium and because it is troublesome to measure slow reactions lasting over a month. The equations just given show that a thousand-fold variation in k changes the temperature effect (k_{308}/k_{298}) by only about 20%. As long as k varies only from 10^{-2} to 10^{-6} and s varies only from 10^{13} to 10^{14}, k_{308}/k_{298} must fall in the neighborhood of 3 or 4.

Although the velocities of related reactions may vary a hundred-fold or more, as in the case of the hydrolysis of different esters, the temperature effects are very closely the same.[10] All these esters react at the same bond and infra-red absorption spectra show that the oscillation frequencies

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[10] Rice, Taylor's "Treatise on Physical Chemistry," D. Van Nostrand Co., New York. 1924, p. 927.

(corresponding to s) at a bond are only slightly changed by introducing more atoms into the molecule. It has been shown that if s remains constant, the value of E and hence k_2/k_1 cannot change materially as long as k varies only a thousand-fold or less.

The constant s appears to be a universal constant within certain limits for unimolecular reactions, Christiansen and Kramers[11] and Polanyi[2] have collected data from a large number of reaction rate experiments and they have shown that E/T and k have such values that s varies only from about 10^{12} to 10^{14}. The results of the present investigation are interesting in this connection. In the earlier work in this Laboratory by Lueck and by the present authors, variations of 1000 to 2000 calories were found in the critical energy, E, for nitrogen pentoxide decomposition in different solvents. The experimental work had been done so carefully and the constants were so reproducible and so satisfactorily unimolecular that these variations were accepted without question. Only after discovering the concentration effect described elsewhere in this communication and after taking special precautions was it established that although the constants varied as much as 100% in the different solvents, the values of k_2/k_1 and hence the critical increments were constant within the limit of experimental accuracy. In the earlier work E varied 10% on account of experimental error in the value of k in Equation 4, and since k was closely fixed by experiment, s varied over seventy-fold. Experimental improvement reduced this variation from 70 to 2 or **3.**

Extraordinary care is necessary in determining k if its temperature coefficient is to be used in calculating E or s. It seems probable that in more complicated reactions or in velocity experiments where the rate is less accurately known, some of the deviations in E and s recorded in the literature may be attributed to experimental error. In fact, the form of the Arrhenius equation is such that in many cases where the data are not very accurate and the "constants" are not constant, the value of E can be calculated more accurately with Equation 2 from k at one temperature on the assumption that s is about 5×10^{13}, than it can be calculated in the usual way from the k's at two temperatures in Equation 4.

The constancy of s in all reactions is in accord with the idea that it represents an oscillation frequency between atoms and is related to absorption bands in the near infra-red. A frequency of 5×10^{13} corresponds to 6μ and almost all organic and inorganic compounds have absorption in this region corresponding to valence bonds which are broken when the molecule decomposes.

One more relation has been noted,[12] namely, that E/RT is approximately constant for many reactions if T is taken so that the different reactions have

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[11] *Christiansen and Kramers, Z. physik. Chem., 104, 451 (1923)*

[12] *Hinshelwood, Chem. Rev, 3,247* (1926)

the same value of k. For example, the specific decomposition rate for nitrogen pentoxide is 0.00158 at 328° absolute and for nitrous oxide it is 0.00150 at 562° absolute. For the former reaction E is 24,700 and $E/RT = 38.0$, while for the latter $E = 68{,}500$ and $E/RT = 41.4$. If k is the same by selection and s is an approximate constant (about 5×10^{13}) representing the natural oscillation frequency of atoms or groups of atoms, then by Equation **3,** E/RT must be a constant. Slight variations in s and hence in k are to be expected because the oscillations will vary somewhat for different atomic groups.

Solvent Effect.—As recorded above, the decomposition rate of nitrogen pentoxide is changed by filling up the empty space between the nitrogen pentoxide molecules in the gas phase with molecules of an inert solvent. Thus far no inert solvent has been found which increases the velocity by more than 100% and none has been found which appreciably decreases the decomposition rate. Large differences in the specific decomposition rate have been found in some cases but these are due to definite chemical reactions with the solvent and they are described in the next communication.

The concentration effect is to be regarded as a special case of a solvent effect in which liquid nitrogen pentoxide is the solvent. Nothing is known of the properties of liquid nitrogen pentoxide[13] and it will be very difficult ever to get direct information because at temperatures above its sublimation point (35°)[14] where it might exist in the liquid phase, it decomposes rapidly and the liquid N_2O_4 formed in the decomposition would dissolve the nitrogen pentoxide and contaminate it. It may be concluded, however, that liquid nitrogen pentoxide would be very much like nitrogen tetroxide because the latter has been shown in this communication to be just as effective as the former in increasing the decomposition rate and maintaining the unimolecularity of the constant over the whole range of decomposition.

Extrapolation to the zero concentration axis should give the maximum solvent effects under conditions where each nitrogen pentoxide molecule is isolated from other nitrogen pentoxide molecules but each is surrounded completely by the solvent molecules. The solutions are sufficiently nearly ideal so that the values at infinite dilution will not be expected to differ much from those for the dilute solutions used here.

Extrapolation to 100% nitrogen pentoxide is not significant on account of the limited solubility, but if the concentrated solutions could exist, the solvent effects would be minimized and all solutions would behave alike, probably much like the solution in liquid nitrogen tetroxide. The concentration curves for all solvents in concentrated solutions would then coincide with the curve for N_2O_4 (Fig. 2).

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[13] The liquid nitrogen pentoxide described in the early literature was probably a solution in N_2O_4 or water.

[14] Daniels and Bright, THIS JOURNAL, 42, 1139 (1920).

The manner in which the solvent atmosphere affects the decomposition rate is important. According to the Arrhenius equation it can affect k either by changing s, the frequency of atom oscillation, or by changing E, the energy of activation. The authors take the view that E is changed rather than s, because a **100%** change in s is required to double k and only a change of **425** calories in **E** is required. The former is quite unlikely. Infra-red absorption bands may shift slightly when new atoms are introduced into the molecule and they may shift slightly in different solvents, but they do not give anything like a **100%** shift. Nitrogen pentoxide absorption bands in the infra-red do not show any shift as great as 0.05μ when dissolved in these solvents.[15]

A change of **425** calories per mole in the heat of activation on the other hand is easily possible. For example, if a compound is formed between nitrogen pentoxide and the solvent with the absorption of heat, the average heat content of the molecules will be increased, the difference (the critical increment, E) between this and the heat content of the activated molecules will be decreased and k will be increased. It is possible that heat effects in other parts of the molecule away from the bond which breaks to give decomposition may obscure the heat effect which is concerned with the reaction. It is possible also that the solvent may quench activated molecules and involve reactions with activated molecules rather than with average molecules. In these cases the heat of solution may not be significant. The thermochemistry of nitrogen pentoxide and its solutions is being investigated in this Laboratory.

Activities.—The experimental data in saturated solutions offer an unusually favorable means of distinguishing between the use of total concentrations and activities in reaction rate measurements. Neither is completely satisfactory. Crystalline nitrogen pentoxide, gaseous nitrogen pentoxide and saturated solutions in the various solvents are all in equilibrium and the escaping tendency of simple N_2O_5 molecules or vapor pressure is the same in every case, but the total concentrations in moles per liter are widely different.

The gas phase may be considered as a special case of solution in which the vacuum acts as solvent. At saturation the increased solubility in solvents over that in vacuum may be attributed for the sake of concreteness to a complex between the nitrogen pentoxide and the solvent, as follows

$$\text{Crystalline } N_2O_5 \rightleftarrows \text{gaseous } N_2O_5 \rightleftarrows \text{simple } N_2O_5 \text{ molecules in solution} \rightleftarrows \text{solvated molecules } (N_2O_5\cdot\text{solvent})$$

The present discussion is not concerned with the type of complex or whether it is chemical or physical in nature.

The experimental facts connected with the decomposition in saturated solutions are summarized in Table V, where k, the specific decomposition

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[15] Daniels, THIS JOURNAL, 47, 2856 (1925)

rate, in the saturated solution is given by the expression $(1/c)\ (-dc/dt)$, C_s is the solubility in mols per liter, and r is the rate of decomposition per liter $-dc/dt$.

TABLE V

DECOMPOSITION IN SOLUTION OF NITROGEN PENTOXIDE WHICH IS IN EQUILIBRIUM WITH CRYSTALLINE NITROGEN PENTOXIDE AT 15°

		N_2O_5 saturating	C_s =	r =	k =
Crystalline N_2O_5	⇆	**Vacuum (gas phase)**	0.0102	0.0080×10^{-5}	0.79×10^{-5}
	⇆	**Liquid CH_3NO_2**	**4.38**	5.92×10^{-5}	1.35×10^{-5}
		Liquid CCl_4	**4.78**	**8.76×10^{-5}**	1.83×10^{-5}
	⇆	**Liquid N_2O_4**	..	....	1.59×10^{-5}

If the activity determines the reaction rate, the evolution of oxygen ($-dc/dt$ per liter) should be the same in all cases because the escaping tendency is the same in all. A glance at the table shows that this situation is far from the truth. Such a result would be obtained if the solvated molecules did not decompose at all.

If the total concentrations determine the decomposition rate, then the *specific* reaction rates, k, should be the same in all solvents. Again, the tables show that this cannot be the case. Such a result would be obtained if all the molecules, solvated and unsolvated, decomposed at the same rate.

Obviously both these views are incomplete. Solvated molecules apparently do decompose but they do not decompose at the same rate as the unsolvated molecules. If they decompose faster, k will be larger and if they decompose more slowly, k will be smaller. The experimental facts show that k is increased by the addition of these solvents and the solvated molecules must be decomposing faster, but apparently not more than twice as fast as the simple molecules. Nitromethane gives a very slight lowering of k and this fact suggests that the solvated molecules may be decomposing very slightly more slowly than the simple molecules.

The case of the solid crystalline nitrogen pentoxide is interesting. It does not decompose at all. Its heat of sublimation—14,600 calories[15]—is added to the critical increment, E.

In other words, a molecule must acquire $24{,}700/(6 \times 10^{23})$ calories of energy more than an average gas molecule before it can become activated; but it must acquire $(24{,}700 + 14{,}600)/(6 \times 10^{23})$ calories of energy more than an average molecule in the crystal lattice. This value of E is so large that the crystal would have to be heated up to 194° on the basis of Equation **3** before the specific decomposition rate would be equal to that in the gas phase at room temperature.

Summary

1. Using an all-glass apparatus the decomposition of nitrogen pentoxide has been measured at various temperatures in the following inert solvents, nitrogen tetroxide, ethylidene chloride, chloroform, ethylene chloride, carbon tetrachloride, pentachloro-ethane, bromine, "vacuum" and nitromethane.

2. The decomposition is strictly unimolecular in all cases. The specific decomposition rate decreases in the order given above. In nitrogen tetroxide it is about twice as large as in the gas phase.

3. The critical increment, E, calculated from the temperature coefficient of reaction rate is 24,700 calories within the limit of experimental error in every case.

4. The specific decomposition rate is somewhat greater in concentrated than in dilute solutions and yet the unimolecularity is maintained throughout the whole course of the reaction. Apparently N_2O_4 and N_2O_5 are equally effective in accelerating the decomposition.

5. Moisture does not affect the decomposition rate.

6. In a mixed solvent the effects of the solvents are proportional to their mole fractions.

7. The decomposition rate was determined in saturated solutions. The results are of interest in the study of activities.

8. The stability of crystalline nitrogen pentoxide is discussed.

9. The constancy of E in different solvents and the universal constancy of the temperature effect are interpreted on the basis of the Arrhenius equation, $k = se^{-E/RT}$ using the experimental data for nitrogen pentoxide.

10. The factor, s, in the Arrhenius equation was found to be constant when the temperature coefficient of reaction rate was determined with great accuracy. It is predicted that s will approach an approximate constant in nearly all unimolecular reactions as experimental measurements become more accurate. The quantity, s, may be identified with the infrared oscillation frequency at the valence bond which is about to break.

MADISON, WISCONSIN

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

THE DECOMPOSITION OF NITROGEN PENTOXIDE IN CHEMICALLY ACTIVE SOLVENTS

BY HENRY EYRING AND FARRINGTON DANIELS

RECEIVED DECEMBER 26, 1929 PUBLISHED APRIL 7, 1930

In the preceding communication[1] it was shown that the normal decomposition rate of nitrogen pentoxide is not appreciably affected by inert solvents. It was found that the specific decomposition rate might vary from the normal rate in the gas phase to twice the normal rate but that the temperature effect and the critical energy of activation, E, remained the same within the limits of experimental error.

Another group of solvents is described here in which the decomposition rates and their temperature coefficients are quite abnormal. The distinction between "inert" and "chemically active" solvents is a matter only of

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[1] Eyring and Daniels, THIS JOURNAL, 52, 1472 (1930).

degree and the small variations among the inert solvents described before may be due to some slight combination with the solvent. Solvation is quite marked in some of the solvents recorded here and it is shown for example that nitric acid reduces the decomposition to one-twentieth of its normal value and yet the decomposition follows the unimolecular law.

Experiments on saturated solutions in the preceding communication were interpreted to indicate that the solvated molecules studied there decomposed slightly faster than the normal molecules. In the present communication other types will be presented, those in which the solvated molecules do not decompose, those in which the solvated molecules decompose at once into new products and those in which the normal decomposition rate is accelerated.

The experimental technique and the method of calculation were the same as those described in the preceding report. Nitrogen pentoxide in solution was sealed off in a small bulb of 5 cc. and shaken violently in a thermostat. The rate of evolution of oxygen was measured with the help of a gas buret connected through a flexible glass spiral.

Experimental Results

Nitric Acid.—Nitrogen pentoxide was dissolved in *3* cc. of 96% nitric acid so that the final concentration was about 0.003 mole of N_2O_5 in 0.07 mole of HNO_3, assuming that the total gas evolved is a measure of the nitrogen pentoxide content.

DATA AT 45°

Time, sec.	0	687	1069	2474	6896	7551	23,876	w
O_2, cc.	0	061	096	185	496	533	1371	37.48
k X 10^5		236	208	1.76	205	175	1 83	

In a second experiment the rate of oxygen evolution was determined at 15 and 35° and the critical energy of activation, E, was found to be 28,300 calories.

As the ratio of N_2O_5 to HNO_3 increased the specific decomposition rate increased, and when the HNO_3 was present only in small amounts it was without noticeable effect. The nitric acid itself showed no appreciable decomposition. The experiments were in agreement with the observation that the addition of a little water to a solvent has no effect on the specific decomposition rate in solution except in special cases (as with carbon disulfide). Rice and Getz,[2] using a titration method, found that nitrogen pentoxide decomposed about one-tenth as fast in the nitric acid as in the gas phase under their conditions, but they did not obtain data for calculating E.

The large value of E and the large temperature coefficient of decomposition rate have the effect of making the nitrogen pentoxide dissolved in nitric

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[2] Rice and Getz, J. *Phys. Chem.*, 31, 1572 (1927).

acid appear quite stable at 15° even though at 45° it decomposes rather rapidly.

Propylene Chloride.—The propylene chloride, obtained from the Eastman Kodak Company, was distilled and dried with phosphorus pentoxide. The data are as follows and the calculated value of E is 27,000 calories.

DATA AT 20°

Time, sec.	0	807	1390	1832	2097	2653	2917	∞
O_2, cc.	0	0.38	0.62	0.81	0.92	1.14	1.24	18.22
$k \times 10^5$		0.261	0.231	0.246	0.238	0.230	0.222	...

DATA AT 35°

Time, sec.	3140	3225	3511	3620	4309	
O_2, cc.	4.00	4.34	5.34	5.73	7.82	
$k \times 10^5$	.....	2.32	2.11	2.26	2.08	
Time, sec.	5470	6077	6577	6730	13.64	∞
O_2, cc.	10.72	12.16	13.04	13.31	19.50	21.40
$k \times 10^5$	2.07	2.39	2.00	2.14	2.10	

The oxygen evolved was free from carbon dioxide. Another less consistent experiment over the same temperature interval gave 28,200 calories for E, and it may be concluded that the critical energy of activation is considerably larger than the 24,700 obtained for the gas phase and for the decomposition in inert solvents. Other data gave 4.13×10^{-5} at 40° and 7.35×10^{-5} at 45° but these data are not suitable for calculating E, as explained in the preceding communication, because the concentrations were not the same in the two experiments.

Carbon Disulfide.—The decomposition of nitrogen pentoxide in carbon disulfide solution is complicated by the oxidation of the solvent and the oxygen evolved contains carbon dioxide and sulfur dioxide. The rate of oxidation is greatly affected by traces of water. In one experiment at 15° when gas was being evolved very slowly, the addition of a small drop of water produced 5 cc. of gas in five minutes and then the reaction slowed down. Three more drops of water caused the evolution of an additional 10 cc. of gas in about two minutes and 5 drops gave a still more violent action, the reaction in each case lasting only for a short time until the nitric acid was used up. The gas consisted chiefly of carbon dioxide and sulfur dioxide and it is evident that carbon disulfide is oxidized rapidly by nitric acid and very slowly by nitrogen pentoxide. Pure nitric acid and carbon disulfide react instantly with great violence.[3]

It was found also that carbon disulfide vapor added to gaseous nitrogen pentoxide gives an abnormal increase in pressure,[4] probably on account of oxidation of the carbon disulfide.

[3] A. C. Andrews, B.S. Thesis, University of Wisconsin, 1924.

[4] Busse and Daniels, THIS JOURNAL, 49, 1259 (1927).

In spite of the complications introduced by the oxidation of the solvent, the data with dry carbon disulfide gave satisfactory constants when calculated by the unimolecular formula, but the results obtained did not check with those obtained several years before and no confidence can be placed in the absolute values of k nor of E.

Iodine.—Iodine in carbon tetrachloride is quickly oxidized by nitrogen pentoxide giving a precipitate of iodine pentoxide. The rate of the reaction has been studied colorimetrically[5] and the reaction is much faster than the normal decomposition rate of nitrogen pentoxide. The reaction at 0° is practically finished in a few minutes. At higher temperatures some oxygen is liberated.

Acetone.—When nitrogen pentoxide is dissolved in acetone, gas is evolved very slowly. It is not oxygen, however, and a unimolecular reaction constant cannot be calculated from the rate of gas evolution.

One typical analysis of the gas gave **25.0** cc. of CO_2, **24.0** cc. of N_2O and **1.0** cc. of oxygen. Carbon dioxide and oxygen were determined in an Orsat apparatus and the density of the residual gas was determined by expelling the gas into a toy rubber balloon tied to the apparatus. The neck of the balloon was then carefully tied off and the balloon was weighed. The 24 cc. at 740-mm. pressure and 25° weighed **0.014** g. in air, giving a molecular weight **14.6** greater than air $(28.9 + 14.6 = 43.5)$. In a second experiment 24.2 cc. of gas weighed **0.0141** in air, giving again a molecular weight of **43.5.** The chemical inactivity and the density showed that the residual gas was nitrous oxide. The chief product in the liquid phase was acetic acid together with a small amount of an unidentified white crystalline solid moderately soluble in water and alcohol.

The reaction between acetone and nitric acid (95% HNO_3) gave the same gaseous products in the same proportions as the reaction with nitrogen pentoxide. McIntosh[6] showed the existence at low temperatures of an equimolecular compound of nitric acid and acetone.

When nitric acid (95% HNO_3) at room temperature is added rapidly to acetone, the latter bursts into flame, but if it is added slowly at 0° no visible reaction occurs. The results may be explained by assuming that the molecular compound between acetone and nitric acid evolves sufficient heat to start the oxidation reaction, which is violently exothermal. The temperature is raised and the reaction is accelerated, whereupon the heat is generated faster and the process continues until the reaction is so fast as to simulate an explosion. The oxidation reaction proceeds normally at 35° provided there is sufficiently rapid shaking to dissipate the heat evolved in the reaction. In one case when the shaking of a bulb containing approximately 2 cc. of nitric acid (95%) and 2 cc. of acetone was discontinued for a

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[5] T. Nash, B.S. Thesis, University of Wisconsin, 1925.

[6] McIntosh, THIS JOURNAL, 27, 1013 (1905).

few minutes a violent explosion occurred although previously the reaction had been proceeding slowly and smoothly. Explosions occurred also when a considerable quantity of nitrogen pentoxide was dissolved in acetone at room temperature but small quantities dissolved without apparent reaction.

The chief reactions appear to be

$$CH_3COCH_3 + HNO_3 = CH_3COCH_3{\cdot}HNO_3$$
$$CH_3COCH_3{\cdot}HNO_3 + HNO_3 = CH_3COOH + CO_2 + N_2O + H_2O$$

This equation gives carbon dioxide and nitrous oxide in equal quantities and acetic acid as the product in solution and it suggests that the reaction is bimolecular.

To determine whether the reaction is bimolecular, as indicated, 2.06 cc. of 95% nitric acid was added to 2.06 cc. of dry redistilled acetone. The solution evolved gas at the rate of 0.00143 cc. per second or at the rate of 3.43×10^{-4} cc. per sec. per cc. To this volume of nitric acid and acetone was added 4.12 cc. of nitromethane as an inert solvent. Gas was then evolved at the rate of 0.00054 cc. per 8.24 cc. of solution. The two measurements were made at 20° with ample shaking and in immediate succession so that no appreciable amount of material decomposed between measurements. Since the concentration of the reacting constituents was half as much in the diluted solution as in the original solution, the rates should be in the ratio of 4 to 1 if the reaction is bimolecular. Actually they are in the ratio of 3.43/0.655 or 5.2 and this agreement is sufficiently close, considering the nature of the assumptions, to conclude that the reaction is bimolecular.

Theoretical Discussion

The experiments described in these two communications illustrate various ways in which the decomposition of nitrogen pentoxide may be affected by solvents. An extreme case of chemical reaction with the solvent might be illustrated by the solution in nitrobenzene. Stable products, dinitrobenzene and nitric acid, are formed at once and no further change occurs. At the other extreme are the inert solvents described in the preceding communication, which have very little effect on the decomposition rate. Probably there is slight solvation, however, in some of these "inert" solvents and the solvated molecules of nitrogen pentoxide decompose at a different rate. In propylene chloride this solvation appears to be carried to a considerable extent so that the critical energy of activation, E, is considerably larger than in the inert solvents.

Solvation can lead to an increased decomposition rate as already shown or it can lead to a decreased decomposition rate as in the case of nitric acid. Part of the molecules of nitrogen pentoxide are apparently locked up in stable complex molecules of the form $N_2O_5{\cdot}nHNO_3$. Although the specific decomposition rate is only about one-twentieth as large, it still follows the unimolecular law because the number of simple molecules which decompose is always proportional to the total concentration of nitrogen pentoxide at any time and this is the criterion of a unimolecular reaction.

The nitric acid solution may be treated mathematically on the assumption that the slow rate is due to the existence of an equilibrium number of stable complex molecules. The energy of activation, 28,300 calories, is 3600 calories greater than the energy of activation in the gas phase or in inert solvents as shown below, and the following reaction may be written.

$$N_2O_5{\cdot}n\mathrm{HNO_3} = N_2O_5 + n\mathrm{HNO_3};\ \Delta H = 3600$$

The equilibrium constants for this reaction may be written

$$K = \frac{C^n_{\mathrm{HNO_3}}\, C_{\mathrm{N_2O_5}}}{C_{\mathrm{N_2O_5}\cdot n\mathrm{HNO_3}}}$$

and since $AF = -RT \ln K$ and $AF = AII - TAS$

$$\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

where *F* is free energy, **11** is heat content, *S* is entropy and T is absolute temperature.

$$\frac{C^n_{\mathrm{HNO_3}}\, C_{\mathrm{N_2O_5}}}{C_{\mathrm{N_2O_5}}{\cdot}n\mathrm{HNO_3}} = e^{\Delta S/R}\, e^{-\Delta H/RT}$$

The rate of decomposition is given by the expression

$$\frac{-\mathrm{d}\, C_{\mathrm{N_2O_5}}}{\mathrm{d}t} = kC_{\mathrm{N_2O_5}} = \frac{kC_{\mathrm{N_2O_5}\cdot n\mathrm{HNO_3}}}{C^n_{\mathrm{HNO_3}}}\, e^{[(\Delta S/R)\ -\ (\Delta H/RT)]}$$

k is the fraction of the nitrogen pentoxide molecules decomposing per second and by the Arrhenius equation

$$k = se^{-E/RT}$$

where *s* is a constant and E is the critical energy of activation. Then

$$\frac{-\mathrm{d}\, C_{\mathrm{N_2O_5}}}{\mathrm{d}t} = \left(s\, \frac{C_{\mathrm{N_2O_5}\cdot n\mathrm{HNO_3}}}{C^n_{\mathrm{HNO_3}}}\, e^{\Delta S/R}\right) e^{-(E\, +\, \Delta H)/RT}$$

In solutions containing a large excess of nitric acid solvent, the quantity in the parentheses is nearly proportional to $C_{\mathrm{N_2O_5}}$ and since A S changes but slightly with temperature, the quantity is nearly independent of temperature. The value of $E + \Delta H$ may then be calculated with fair accuracy from the experimentally determined temperature coefficient of the reaction rate in the usual manner.

E + A H was found to be 28,300 and E for simple nitrogen pentoxide molecules has been found repeatedly to have the value 24,700. The heat of formation of the solvated molecules is then 3600 calories.

The three additional solvents described here were studied because they involve definite chemical interaction with the solvent to give new products. In all cases the apparent reaction is more rapid than the normal decomposition. Carbon disulfide is oxidized rather slowly, while iodine in solution is oxidized rapidly to iodine pentoxide. In both cases some of the nitrogen pentoxide decomposes spontaneously in the normal way to liberate oxygen.

The decomposition in acetone is interesting although seriously complicated by the formation of a solvated molecule which reacts to give an entirely different set of products. The reaction is probably typical of many organic reactions. It is further complicated by the fact that water is produced as one of the products and, it in turn, forms nitric acid, which reacts faster with the acetone. The reaction between nitrogen pentoxide and any substance containing hydrogen which is oxidized should be considered also as a reaction with nitric acid, and, in fact, the latter may be the predominating reaction on account of its greater speed.

These studies are of interest in connection with the use of activities in reaction rate calculations. Concentration measurements give both solvated and unsolvated molecules while activities may give the concentration of the unsolvated molecules alone. If the solvated molecules do not decompose (as in this case of solution in nitric acid), the rate of decomposition should be proportional to the activities of the unsolvated molecules. If concentrations are used in the calculations, the reaction rate will still follow the unimolecular formula in dilute solutions because the concentration of unsolvated molecules is always proportional to the total concentration, but the specific decomposition rate calculated in this way will be abnormally low.

If the solvated molecules decompose faster than the unsolvated molecules, as in the case of solvents described in the preceding communication, the specific decomposition rate will be too high, and the substitution of activities for total concentrations will not help.

Summary

1. Nitrogen pentoxide dissolved in nitric acid decomposes very slowly and follows the unimolecular formula. The results can be explained on the assumption of stable solvated molecules in equilibrium with the nitrogen pentoxide. The decomposition rate has a very high temperature coefficient. $E = 28{,}300$ and $k_{45^\circ} = 1.97 \times 10^{-5}$.

2. In propylene chloride, nitrogen pentoxide decomposes without apparent action on the solvent. The temperature coefficient is abnormally high, giving E a value of 28,000. At 35° $k = 2.3 \times 10^{-5}$.

3. Carbon disulfide is oxidized by dissolved nitrogen pentoxide but the latter also decomposes with the liberation of oxygen. A little water produces nitric acid and gives a much more rapid oxidation.

4. Iodine in solution is rapidly oxidized by nitrogen pentoxide but some nitrogen pentoxide decomposes independently.

5. With acetone nitrogen pentoxide or nitric acid forms an addition product which reacts further to give nitrous oxide, carbon dioxide and acetic acid.

6. The concept of activities is discussed in connection with the decomposition rate in the various cases of solution.

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

SILVER ION CATALYSIS OF PERSULFATE OXIDATIONS. V. A QUANTITATIVE STUDY OF THE OXIDATION OF AMMONIA[1]

BY CECIL V. KING AND F. L. GRISWOLD

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Introduction

It was first shown by Marshall[2] that ammonia is oxidized to free nitrogen by persulfate, in the presence of silver salts. Marshall assumed that this reaction was quantitative, or nearly so, without making any extended investigation of the matter; while he found a trace of oxygen in the gas evolved, he attributed this to the accidental admixture of some air. Marshall also showed that ammonium ion, in neutral or acid solution, is oxidized to nitrate ion,[3] and this he proved to be practically quantitative except in strongly acid solution.

Yost, in a study of the velocity of the oxidation of ammonia by persulfate and silver ions,[4] assumed that the oxidation to free nitrogen was quantitative in solutions containing ammonia with or without added alkali (KOH), and the same assumption was made by King[5] in the first paper of this series, without further inquiry.

The original purpose of the present investigation was to determine the concentrations of ammonia and ammonium ion, or the hydrogen-ion concentration, of the solutions in which the oxidation to nitrate begins to replace the oxidation to free nitrogen. However, as will be seen below, it unexpectedly developed that the production of nitrogen is quantitative in a very limited concentration range, and, it therefore, became the purpose of this work to investigate the effect of various substances on the amount of nitrogen evolved.

It is assumed that when ammonia or ammonium ion is oxidized, only the two substances mentioned are produced, according to the following equations

$$2NH_3 + 3S_2O_8^{=} \longrightarrow N_2 + 6SO_4^{=} + 6H^+ \qquad (1)$$

$$NH_4^+ + 4S_2O_8^{=} + 3H_2O \longrightarrow NO_3^- + 8SO_4^{=} + 10\,H^+ \qquad (2)$$

It is unlikely that other possible products could exist in appreciable amounts in the presence of persulfate and silver ions. While oxygen is produced by the action of persulfate on water, the reaction is so slow as to be negligible under the conditions of these experiments.

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[1] This paper summarizes a thesis presented by F. L. Griswold to the Graduate Faculties of New York University in partial fulfilment of the requirements for the degree of Master of Science.

[2] Marshall, *Proc. Roy. Soc.* Edinburgh, 23, 163 (1900).

[3] Marshall, *ibid.*, 24, 88 (1902).

[4] Yost, THIS JOURNAL, 48, 374 (1926).

[5] King, *ibid.*, 49, 2689 (1927).

It will be seen that after the persulfate has all disappeared, the extent of both reactions can be estimated by any one of three methods: (1) estimating the nitrate produced, (2) titrating the unoxidized and un-neutralized ammonia remaining, or the acid produced, or (3) measuring the volume of nitrogen produced. Of these, the third was selected as being sufficiently accurate and by far the easiest.

Materials and Experimental Procedure

Potassium persulfate was recrystallized until free from sulfate. C. P. ammonia water was diluted to the desired strength and standardized against hydrochloric acid. Ammonium nitrate was recrystallized and dried in a desiccator. Standard solutions of silver nitrate, potassium nitrate and sodium hydroxide were prepared from C. P. materials.

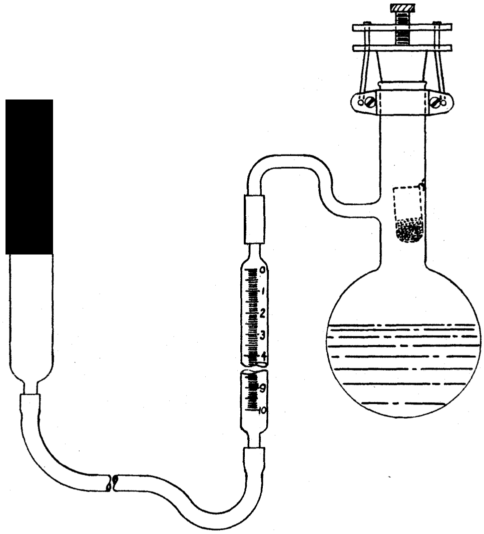

Fig. 1.

Standard solutions of the reagents desired, except the persulfate, were pipetted into the reaction flask shown in Fig. 1 and made up to 100 cc. The exact amount of potassium persulfate (0.1809 *g.)* to liberate 5 cc. of nitrogen at standard conditions was carefully weighed into a glass capsule and hung on a platinum loop in the neck of the reaction flask. The flask was sealed, the persulfate shaken down and dissolved, and the apparatus allowed to stand until no more nitrogen was evolved (usually twenty-four hours were allowed, sometimes forty-eight). The nitrogen volume was noted by readings on the attached gas buret before and after the reaction, and then corrected to 0° and 760 mm. Corrections were made, of course, for change in the total volume of air and nitrogen in the entire gas space (approx. 65 cc.) when there was any change in atmospheric pressure during the experiment, and for the vapor pressure of water and ammonia above the solutions. The flask was thoroughly shaken before the final reading to avoid supersaturation.

All experiments were carried out at 25 ± 0.02° by immersing the entire apparatus in a large thermostat. The particular persulfate concentration to evolve theoretically 5 cc. of nitrogen was chosen because it is close to some of the values used by Yost and by King, and also because with the apparatus chosen this amount was convenient and gave a suitable degree of accuracy (± less than 1% in most of the experiments). While only experiments with this persulfate concentration are reported here, preliminary experiments with other concentrations gave similar results.

Results of Experiments and Discussion

The results of all the experiments are given in Table I and are shown graphically in Fig. 2, where average values of the duplicates given in the table are plotted. The volumes given are cc. of nitrogen (corrected to standard conditions) evolved at 25°, the theoretical value being 5 cc., *i. e.*, if all the persulfate disappeared according to Equation 1. Three concentrations of silver nitrate, 0.04 M, 0.02 *M* and 0.005 *M* were used; 0.04 *M* silver nitrate will, of course, require 0.08 *M* ammonia to form the silver diammonia ion. About 0.0045 *M* ammonia in addition is required for the oxidation by Equation 1 and 0.013 M ammonia to neutralize the hydrogen ion produced, making about 0.1 M ammonia necessary to leave any excess. Some nitrogen is produced with even less than 0.08 M ammonia, but the theoretical amount is not produced even with 0.1 *M* or more concentrated ammonia (see Col. *2* in the table).

TABLE I

CC. OF NITROGEN (CORRECTED TO 0° AND 760 MM.) EVOLVED AT 25° FROM 100 CC. SOLUTION OF CONCENTRATIONS SHOWN. $K_2S_2O_8$ 0.00667 M IN ALL EXPERIMENTS

C_{NH_3}	$AgNO_3$, 0 04 *M*			$AgNO_3$, 0 02 M		$AgNO_3$, 0 005 *M*		$AgNO_3$, 0 0033 *M*
		NH_4NO_3, 0 025 *M*	KNO_3, 0 04 *M*		NH_4NO_3, 0.1 *M*		NH_4NO_3, 0.1 *M*	NaOH
0 0265	1 96		1 73	2 08	3 26	3 67	3 75	(0 1 M)
	1 93		1 78		3 28	2 52	4 19	
	1 99					3 79	4 43	1 85
	1 91					3 77	4 48	1 63
053	2 86	3 13		3 96	4 56	4 12	4 92	(0 04 M)
	2 72	2 72		3 78		4 21	4 87	
	2 30	2 55				3 91		2 16
	2 30	2 53				3 98		2 11
106	3 93	4 11		4 37	4 99	4 41	4 90	(0 1 M)
	4 25	4 47		4 37	4 94	4 36	4 94	2 75
								2 88
265	4 70	4 85		4 43	4 88	4 51	5 05	
	4 75			4 43	4 91	4 62	5 05	
	4 80							
	4 57							
53	4 81	4 79		4 60	4 87	4 54	5 02	
	4 73	4 82		4 59	4 93	4 52	5 02	
		4 80						
4 5						4 13	4 01	
						3 98	4 10	

Thus it appears that ammonia can be oxidized even though the amount in the solution is stoichiometrically unable to satisfy the silver ion, but it is evident that nitrogen alone is not produced ***below*** some definite hydrogen-ion concentration and nitrate ion alone ***above*** this hydrogen-ion concentration. Since the persulfate all disappeared in these experiments, the two reactions must proceed simultaneously, probably from the start. The experiments with lower silver-ion concentrations gave similar results. With 0.02 M silver nitrate, about 0.06 M ammonia is necessary to leave any excess. However, the theoretical amount of nitrogen is not liberated with any ammonia concentration up to 0.53 *M* (Col. 5 in the table). The same is true for 0.005 M silver nitrate (Col. 7 in the table). With low concentrations of ammonia, less silver nitrate gives more nitrogen; with higher ammonia concentrations, the reverse is true.

It was expected that addition of sodium hydroxide would increase the evolution of nitrogen. The last column of the table shows that the reverse is true. No comparative experiments were run with 0.0033 M silver nitrate and no sodium hydroxide, but it can easily be predicted from the table and curves that more nitrogen would be evolved.

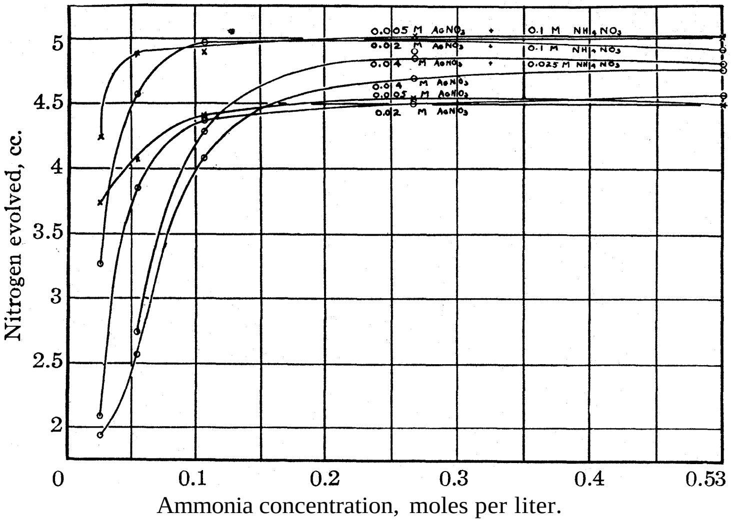

Fig. 2.—Volume of nitrogen evolved at 25° (corrected to 0° and 760 mm.) from 100 cc. of solution containing 0.00667 M $K_2S_2O_8$ and other reagents as shown. The concentration scale is compressed slightly at the extreme right.

According to Marshall[2,3] and experiments described in the first paper of this series, no nitrogen is liberated from a neutral or acid solution of an ammonium salt, and this was verified by experiments carried out by the method used here. The addition of an ammonium salt increases the hydrogen-ion concentration as well as the ammonium-ion concentration. It was, therefore, expected that addition of ammonium nitrate would decrease the amount of nitrogen produced, and increase the proportion of nitrate formed; just the opposite effect was observed, as is shown by the values in Cols. 3, 6 and 8 of the table and by the curves in Fig. 2. This is true for most of the curve with 0.04 *M* silver nitrate, with only 0.025 M ammonium nitrate, and the effect is especially pronounced with the 0.02 M and 0.005 M silver nitrate and 0.1 M ammonium nitrate. It will be noticed that *only these solutions with the lower silver nitrate concentrations and considerable added ammonium nitrate approach the theoretical evolution of* *nitrogen*. In the solutions with 0.02 M silver nitrate the 5 cc. is scarcely reached (within experimental error) but with 0.005 M silver nitrate and 0.1 *M* ammonium nitrate it is certain that for some of the ammonia concentrations the reaction is quantitative according to Equation 1.

It was thought possible that this increase in nitrogen evolution by ammonium nitrate was a general effect that would be produced by the addition of any inert salt. For this reason two experiments were run with the addition of potassium nitrate, but as is seen in Col. 4 of the table, potassium nitrate actually decreases the evolution; the effect of ammonium salts is a specific one.

Some of the values for 0.53 M ammonia are slightly lower than the values for lower ammonia concentrations. The difference is almost within experimental error, but a few experiments with 4.5 M ammonia confirmed the suspicion that the amount of nitrogen produced reaches a maximum and thereafter falls off with increasing ammonia concentration. These results are shown in the table but not on the curves in Fig. 2.

Conclusions

It is impossible to say definitely whether some ammonium ion is oxidized to nitrogen in the slightly alkaline solution (although it is not in neutral or acid solution) and that this accounts for the effect of added ammonium ion, or whether the increase in hydrogen-ion concentration brings about increased oxidation of ammonia itself to nitrogen.

The most obvious conclusion is that Yost and King, in their experiments (referred to above), did not meet the conditions necessary for the theoretical evolution of nitrogen. While the experiments here do not duplicate their concentrations exactly, it is easily seen that even in their experiments with no alkali added the nitrogen evolution could scarcely be over 80% of the theoretical, and with added hydroxide it must have fallen as low as 50%. Yost measured the rate of disappearance of persulfate and consequently the sum of Reactions 1 and 2; King measured the rate of evolution of nitrogen, and assumed in calculating velocity constants that this was proportional to the rate of disappearance of persulfate. Thus their measurements are undoubtedly valid when it is remembered that the slow reaction is probably that between persulfate and silver ions, whether nitrogen or nitrate is produced later, but the fact that neither product is formed quantitatively must always be considered before the results are used for other than comparative purposes.

Summary

Measurements of the volume of nitrogen evolved when ammonia is oxidized by persulfate ion in the presence of silver ion show that: (1) the theoretical amount of nitrogen is produced only under a very limited range of concentrations of ammonia, ammonium ion and silver ion; (2) the

addition of ammonium nitrate increases the volume of nitrogen evolved; (3) the addition of sodium hydroxide or potassium nitrate decreases the amount of nitrogen evolved; (4) although nitrogen is produced when less than enough ammonia is present to form the silver diammonia ion, a large excess of ammonia is necessary to give the maximum nitrogen evolution. With still higher ammonia concentrations the amount of nitrogen produced decreases again. (5) Yost, and King were unjustified in assuming that in their experiments the disappearance of persulfate was due to one reaction only.

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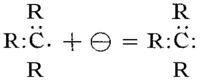
[CONTRIBUTED FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ELECTRON AFFINITY OF FREE RADICALS. I. THE ELECTRON AFFINITY OF TRIPHENYLMETHYL

BY HENRY E. BENT

RECEIVED JANUARY 4, 1930 PUBLISHED APRIL 7, 1930

The elementary process of removing an electron from an atom involves an energy change which is related to both the nuclear charge and the electronic configuration of the atom. Millikan and Bowen[1] have shown the energy to be a linear function of the square of the nuclear charge in systems containing the same number of electrons. A study of the electron affinities of free radicals offers the opportunity of keeping the nuclear charge and the number of electrons constant while studying the effect of varying the groups which share six of the electrons of the atom. Thus in the reaction



$$\begin{matrix} R \\ R{:}\ddot{C}\cdot \\ R \end{matrix} + \ominus = \begin{matrix} R \\ R{:}\ddot{C}{:} \\ R \end{matrix}$$

the measurement of AII for various radicals should enable one to determine to what extent the addition of an electron to an odd molecule to form an electron pair is affected by a change in the configuration of the rest of the electrons in the molecule. This paper describes the procedure and gives the data for triphenylmethyl.

The reaction chosen for study is that of the addition of sodium to triphenylmethyl

$$Na + R = Na^{+} + R^{-}$$

in which R represents triphenylmethyl. The free energy change accompanying this reaction may be obtained directly from the equilibrium constant for the reaction provided experimental conditions can be found for establishing an equilibrium and determining the activities of the various molecular and ionic species. The large deviation from perfect solution shown by sodium amalgams suggested the possibility of using them in

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[1] Millikan and Bowen, *Proc. Nat. Acad Sci.*, **13, 531** (1927).

measuring such equilibria. The activity of sodium in dilute amalgam has been determined recently as a function of the concentration of the amalgam[2] and indicated that sodium amalgams could be used provided the free energy change is of the order of magnitude of 20,000 calories.

The first step is to prove that the reaction is reversible. This was accomplished first by noting that sodium amalgam reacted with triphenylmethyl to give a dark red solution of sodium-triphenylmethyl and that this red color partially disappeared on shaking with mercury and was restored by again shaking with sodium amalgam. Schlenk[3] has recently shown that sodium can be removed from a number of similar compounds by shaking with mercury. As further proof that the reaction is reversible, the equilibrium was approached from both sides and the concentration of the sodium in the amalgam determined by treating with standard acid. Within the limits of the accuracy of the analysis there was no difference between the two results.

A study of the data obtained in this work together with the information which we already have regarding these compounds indicates that there are at least three independent reactions

$$R_2 = 2R \qquad (1)$$
$$Na + R = Na^+ + R^- \qquad (2)$$
$$NaR = Na^+ + R^- \qquad (3)$$

By combining these equations we obtain in addition the following equations

$$Na + R = NaR \qquad (4)$$
$$2Na + R_2 = 2Na^+ + 2R^- \qquad (5)$$
$$2Na + R_2 = 2NaR \qquad (6)$$

Values for the free energy changes for the above reactions have been determined taking the standard state for sodium as the metal at 25°, while for all other molecules or ions the activity has been taken as equal to the mole fraction. Values for the free energy change of Reaction 2, using a number of free radicals, will give the effect of varying valence bonds on the electron affinity inasmuch as the other product is in every case sodium ion in ether.

The absolute value for the electron affinity, however, is to be obtained by studying the reaction in the gaseous state. This may be done by combining the above reaction with the appropriate equations for vaporization, solvation and the ionization potential of sodium to give the electron affinity of triphenylmethyl in the gaseous state. The value so obtained is 59 ± 5 kilogram calories.

Experimental

A weighed amount of triphenylchloromethane is first introduced into a tube (B, Fig. 1) and the apparatus sealed to a line for evacuation. The tube is warmed and sparked during evacuation and the pumping continued

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[2] Bent and Hildebrand, THIS JOURNAL, 49, 3011 (1927).

[3] Schlenk and co-workers, *Ann.*, 463, 1 (1928).

until the pressure measured by a McLeod gage is less than 5 × 10^{-4} mm. A stopcock, not shown, is then opened to allow sodium amalgam to run into Tube B and then a second stopcock through which ether is distilled from a reservoir containing sodium–potassium alloy. The line leading to the above reservoirs and pump is then sealed off and the tube shaken for twelve hours. The two reactions

$$\begin{aligned} \mathrm{Na} + \mathrm{RCl} &= \mathrm{R} + \mathrm{NaCl} \\ \mathrm{Na} + \mathrm{R} &= \mathrm{Na}^{+} + \mathrm{R}^{-} \end{aligned} \tag{7}$$

may be followed by the color change, first to yellow and then to red. The reaction appears to be complete in less than five minutes. However, the solution is clearer if the shaking is continued for several hours. Tilting the tube and cooling Tube A with ice filters the ether solution through the alundum disk sealed in at C. Distillation of the ether back onto the sodium amalgam twice serves to rinse over 99% of the sodium-triphenylmethyl. The tubes are then sealed off at D and mercury run into Tube A through the stopcock which had been previously filled with a little mercury. Tube A is then placed inside of a small thermostat which keeps the tube entirely dark and the whole apparatus is shaken on a special shaker[4] for twelve hours. Tube **A** is then attached by rubber connections to a receiving flask for analysis, the flask evacuated and the ether vapor allowed to force the dilute amalgam into the flask, the process being carried out with the tube still in the thermostat and the mercury coming in contact with none of the rubber connections. The dilute amalgam is then boiled with standard 0.01 M sulfuric acid, in contact with platinum to cut down overvoltage, and the amount of sodium is obtained by titration. The mercury is also weighed and the volume of ether obtained by weighing an equal volume of water.

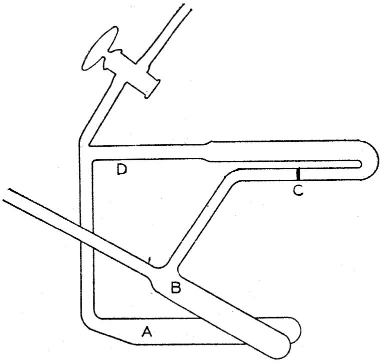

Fig. 1.

Materials

The triphenylchloromethane was prepared from recrystallized carbinol by treating with **dry** hydrogen chloride in dry benzene in the presence of calcium chloride and was recrystallized until the melting point was above 110°. Analysis for chlorine by the Volhard method gave a value which indicated that the material was over 99.9% pure. The compound was kept in the dark in a special bottle provided with a mercury seal and containing a little calcium chloride. Samples could be obtained from this bottle without introducing any air. The final set of experiments used in the calculations was carried out over a period of about a month and the compound again analyzed at the conclusion, giving 99.1% of the calculated amount of chlorine.

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[4] Bent, *Ind. Eng. Chem., Analytical Edition,* 2, 106 (1930).

The ether was stored over sodium–potassium alloy and not used until after the alloy had stopped reacting and remained perfectly bright. It was found possible to use a good grade of rubber stopcock grease on the stopcock of this storage flask provided it was maintained a few degrees above the temperature of the room by a small incandescent bulb placed near it which prevented the ether vapor condensing in the grease.

The sodium was melted and run through a constriction to remove dross and previously washed mercury distilled onto it.

Blank determinations failed to show any correction for impurities in the mercury or sodium or amalgam carried over with ether into the second tube.

Calculation of Results

The experimental data give the weight of triphenylchloromethane, the weight of mercury, the number of gram atoms of sodium removed by the mercury and the volume of ether. Since the sodium amalgam used to convert the chloride into the sodium salt is relatively very concentrated (amalgam in equilibrium with solid amalgam), all of the chloride is converted into the sodium salt during the first shaking. The number of gram atoms of sodium removed by the mercury is, therefore, equal to the number of moles of free radical in dilute solution. Subtracting this from the number of moles of chloride introduced at the beginning of the experiment gives the number of moles of triphenylmethyl ion and of sodium ion. These data together with the volume of ether and weight of mercury give all that is necessary for calculation of the equilibrium constant of Equation 2.

In more concentrated solutions the number of gram atoms of sodium removed by the mercury gives not the number of moles of the free radical (R) but $R + 2R^2/nK_1$ in which K_1 is the equilibrium constant of Equation 1 and n is the number of moles of ether. In the same way the total amount of sodium left in solution gives $R^- + (R^-)^2/nK_3$ in which R^- is the number of moles of triphenylmethyl ion. Values for the equilibrium constants of Equations **1** and **3** were obtained by successive approximations and the results are given in Table I. Unfortunately it is not possible to show by any simple graphical method the determination of these constants, due to the number of constants involved and the analytical necessity of removing as nearly as possible half of the sodium.

The first column gives the number of the run. The second gives the number of gram atoms of sodium removed by the mercury. Subtracting this from the number of moles of triphenylchloromethane gives the number of moles of sodium ion plus any un-ionized salt. The fourth and fifth columns give the number of moles of ether and mercury while the last two give the logarithm of the equilibrium constant of Equation 2. The values obtained in the next to the last column are simply a result of assuming, as a first approximation, no association. A large number of such approximations indicate the values given in the last column to be the most probable with an uncertainty of a power of ten in K_1 and K_3. That the uncertainty in these constants is so large is due first to the fact that the activity of an

TABLE I

VALUES OF EQUILIBRIUM CONSTANTS

Run	G. atoms of Na removed X 10^4	G. atoms of Na left X 10^4	Moles of ether	G. atoms of Hg	Log K_2 $K_1 = \infty$ $K_3 = \infty$	 K_1 = 10-4 K_3 = 10-4
41	0 393	0 432	0 171	0 875	13 68	13 41
46	0.960	0 474	121	0 883	13 13	12 99
42	1 340	0 481	122	1 103	12 96	12 87
43	2 282	1 358	109	1 063	13 40	13 01
44	4 005	3 775	117	1 013	13 77	13 14
32	1 55	0 755	061	0 967	13 47	13 13
33	1 43	0 925	074	1 020	13 65	13 24
34	1 34	0 880	.076	0 908	13 60	13.23
35	1 40	0 790	079	1 025	13 51	13.18
36	3 45	2 78	047	0 952	14 01	13.29
37	0 308	0 208	095	1 083	13 87	13 44
38	0 265	0 352	.168	0 735	13 77	13 52

Runs 39 and 40 were made in very dilute solutions and for this reason involved such large percentage errors as to be of no value. Run 45 showed precipitation, probably of peroxide as a result of a small leak, and was, therefore, also discarded.

ion is not exactly equal to its concentration in even these dilute solutions.[5] In the second place, the amalgams are very dilute, thus introducing a rather large error from the analysis. Finally, very accurate data are necessary in order to determine three constants with any precision. Fortunately there are other means, which are described below, of determining these two constants which confirm the above values.

The first five runs given in the table are considered to be the most reliable. Runs 32 to 35 were carried out at one concentration in order to determine the reproducibility of the results at that concentration, and Runs 37 and 38 for the same reason at a lower concentration; 13.1 is taken as the value of log K_2, the probable error being less than 0.1. However, a variation of K_1 or K_3 by a power of ten affects log K_2 by about 0.5, so that this should be taken as a measure of the accuracy of this figure.

Since A F = $-RT \ln K$ we find the free energy change for Reaction 1 to be +5.5 kilogram calories, (2) −17.9, (3) +5.5, (4) −23.4, (5) −30.3 and (6) −40.3.

K_1 has been determined by Ziegler and Ewald[6] in a variety of solvents and at 25°. Expressing concentrations as mole fraction, K_1 is found to vary from 0.1×10^{-4} to 1.5×10^{-4}, the value 0.5×10^{-4} being very close to that given in many solvents. Unfortunately no measurements were made on ether solutions, but the value is probably not far from 0.5×10^{-4}. This is well within the limit assigned to the probable error of K_1 above.

K_3 cannot be checked so well. Schlenk and Marcus[7] have found the

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[5] Kraus and Bray, THIS JOURNAL, **35**, 1353 (1913).

[6] Ziegler and Ewald, *Ann*, **473**, 163 (1929).

[7] Schlenk and Marcus, *Ber* , **47**, 1664 (1914).

equivalent conductance of sodium-triphenylmethyl in ether to be 4.8 X 10^{-2} for a solution containing 0.4 g. of salt in 40 cc. of ether. This measurement does not permit calculation of the degree of dissociation inasmuch as Λ_∞ is unknown. However, the conductivity is so small as to indicate no large dissociation.

The value of the electron affinity of the free radical in the gaseous state is obtained by adding the following equations

			AF	
$^1/_2$ (R_{2ether} + 2 Na_{solid}	= $2Na^+_{ether}$ + $2R^-_{ether}$)		−15 15	(2)
$Na^+_{ether\ soln}$	= Na_{gas}		+79 9	(8)
$R^-_{ether\ soln.}$	= R^-_{gas}		+27 3	(9)
Na_{gas}	= Na_{solid}		−18 5	(10)
$^1/_2$ (R_{2gas}	= $R_{2liquid}$)		− 4 3	(11)
$R^-_{N=1}$	= $R^-_{N=0.0043}$		− 3 24	(12)
$Na^+_{N=1}$	= $Na^+_{N=0.0043}$		− 3 24	(13)
$^1/_2$ ($2R_{gas}$	= R_{2gas})		− 4 0	(14)
Na_{gas} + R_{gas}	= Na^+_{gas} + R^-_{gas}	A H = ΔF =	+58 87	(15)
Na^+_{gas} + ⊖	= Na_{gas}	A H	−118 0	(16)
R_{gas} + ⊖	= R^-_{gas}	A H	−59.0	(17)

The values for *AF* and *AH* are given in kilogram calories. Values for Equations 8 and 9 are calculated by the method of Born,[8] and are thought to be good to perhaps three kg. cal. for the sodium ion and one kg. cal. for the triphenylmethyl ion. The fact that the dielectric constant is small for ether as compared with water would seem to justify one in expecting the results to be at least as good as in aqueous solution. The radius of the sodium ion is that used by Born for aqueous solutions, while the value for the triphenylmethyl ion is calculated from the molecular volume of triphenylmethane. The difference between the volume of this compound and the ion has been considered to be due to the loss of one hydrogen, calculated by Kopp's law and the addition of one electron. Born[8] has determined the magnitude of the change in volume resulting from the addition of an electron to a number of atoms. Unless the effect on triphenylmethyl is of an entirely different order of magnitude, the mean of these values may be used without introducing any significant error. The value for Equation 10 is calculated from the vapor pressure of sodium at 25°. *AF* for Reactions 11 to 14 is so small that a very rough estimate is all that is necessary. The vapor pressure of hexaphenylethane has been calculated for Reaction 11 by taking the boiling point as 450° and applying Trouton's rule. The assumption that the activity of hexaphenylethane in ether is equal to the mole fraction for supercooled hexaphenylethane introduces an error which is probably less than 0.5 kilogram calorie.[9] Reactions 12 and 13 are necessary in order that the concentration in the gaseous state may be one atmosphere, a mole fraction of 0.0043 in ether giving a concentration of one mole in a molar volume. The value for Reaction 14

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

[9] Hildebrand, "Solubility," The Chemical Catalog Co , New York, 1924, p. 156.

is obtained by taking the value in ether solution and correcting for the change in activity in passing to the gaseous state. Several assumptions were made and checked on nitrogen dioxide and formic acid. Inasmuch as an effort is being made to measure this reaction in the gaseous state and also the vapor pressure of hexaphenylethane, it is perhaps unnecessary to discuss the method further. Reaction 15, which is the sum of the above eight equations, gives the free energy change for concentrations of one atmosphere. However, since there is no change in entropy for such a gaseous reaction, the various species on both sides of the reaction having the same weight, this value may also be taken as *AH* for the reaction. Combining with Reaction 16 then gives the electron affinity of the free radical as 59 kilogram calories with a probable error of about five kilogram calories. The error in *AF* for Equation *8* is thought to be less than three kilogram calories and for all of the other reactions less than one kilogram calorie.

The author takes pleasure in expressing his appreciation of the interest and suggestions of Dr. W. H. Carothers.

Summary

The addition of sodium to triphenylmethyl has been found to be a reversible reaction. *AF* for this reaction has been determined and also for the dissociation of hexaphenylethane and sodium-triphenylmethyl. The electron affinity of triphenylmethyl in the gaseous state has been found to be 59 ± 5 kilogram calories.

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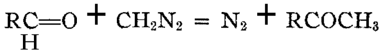
[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, UNIVERSITY OF BRISTOL]

THE ACTION OF DIAZOMETHANE ON SOME AROMATIC ACYL CHLORIDES. V. THE MECHANISM OF THE REACTION

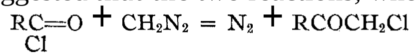
BY T. MALKIN AND M. NIERENSTEIN

RECEIVED MARCH 28, 1929 PUBLISHED APRIL 7, 1930

In Part III of this series[1] an attempt was made to coordinate the Schlotterbeck reaction[2] with what has now become known as the Nierenstein reaction.[3] It was suggested that the two reactions, where X = H (Schlotterbeck) and X = Cl or Br (Nierenstein) proceed as follows



$$\underset{\text{H}}{\text{RC}}\text{=O} + \text{CH}_2\text{N}_2 = \text{N}_2 + \text{RCOCH}_3$$



$$\underset{\text{Cl}}{\text{RC}}\text{=O} + \text{CH}_2\text{N}_2 = \text{N}_2 + \text{RCOCH}_2\text{Cl}$$

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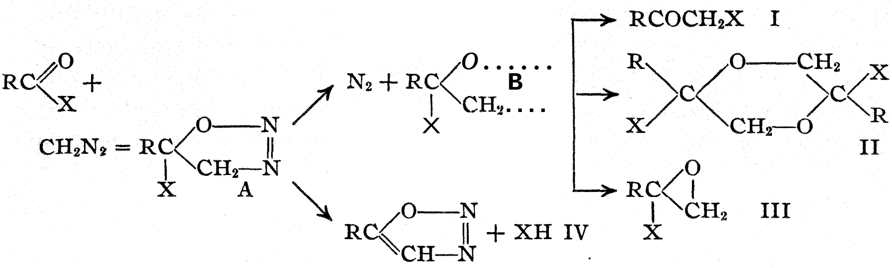
[1] Lewis, Nierenstein and Rich, THIS JOURNAL, 47, 1728 (1925).

[2] Schlotterbeck, *Ber.*, 40,479 (1907).

[3] (a) Clibbens and Nierenstein, *J. Chem. Soc.*, 107, 1481 (1915); (b) Nierenstein, *ibid.*, 117, 1153 (1920); *(c)* Nierenstein, Wang and Warr, THIS JOURNAL, 46, 2554 (1924); (d) Kahil and Nierenstein, *ibid.*, 46, 2557 (1924); (e) Lewis, Nierenstein and Rich, *ibid.*, 47, 1728 (1925); (f) Dale and Nierenstein, Ber., 60, 1026 (1927); (g) Malkin and Nierenstein, *ibid.*, 61,797 (1928).



This view was supported by the fact that not only o-halogenated acetophenones (I) but that also dihalogenated dioxans (II) are produced under these conditions. Since the publication of this paper Arndt and his collaborators[4] have succeeded in obtaining compounds derived from Formula III, whereas Meerwein and Burneleit[5] have shown that acetone, where X = CH_3, yields with diazomethane products derived from both Formulas I and III.

A very interesting extension of the reaction was described by Arndt and his collaborators,[6] who succeeded in isolating products derived from Formula IV due to the elimination of XH (for example, HCl) in the intermediary substance A. Arndt's work thus completed the whole cycle of possibilities, indicated above, and it is to be regretted that he has unfortunately assigned to his products the general formula $RCOCHN_2$, although he finds that they do not give phenylhydrazones. It is evident from the literature[7] that it is quite an open question whether the products under consideration are to be regarded as true diazo compounds, as supposed by Arndt, or as cyclic diazo-anhydrides (IV), as suggested by Angeli,[8] and seriously considered by Staudinger[9] and Wieland.[10] The fact that these nitrogen-containing compounds are obtained under the above-mentioned conditions seems to indicate that they are diazo-anhydrides (IV), and not true diazo compounds, and this is confirmed by their resistance to iodine, as already pointed out by Wolff.[11] The statement that the

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[4] Arndt and Eistert, *Ber.*, 61, 1118 (1928); Arndt, Eistert and Amende, *ibid.*, 61, 1949 (1928).

[5] Meerwein and Burneleit, ibid., 61, 1840 (1928).

[6] Arndt, Eistert and Partale, *ibid.*, 60, 1364 (1927); Arndt and Amende, *ibid.*, 61, 1122 (1928).

[7] Meyer–Jacobson, "Lehrbuch der Organischen Chemie," 1920, Vol. III, Pt. III, p. 624. Berlii and Leipzig.

[8] Angeli, Ber., 26, 1715 (1893).

[9] Staudinger, "Die Ketene," Stuttgart, 1912, p. 30.

[10] Wieland, "Die Hydrazine," Stuttgart, 1913, pp. 96,103. The following quotation from Wieland (p. 103) summarizes his views: "Eine entscheidende Lostrennung der bisher als Diazoanhydride aufgefassten Verbindungen von den Diazokörpern wird voraussichtlich erst dann mit aller Sicherheit moglich sein, wenn man in einern Fall die beiden Isomeren erhalten hat."

[11] Wolff, *Ann.*, 325, 142 (1902).

nitrogen-containing compound which Bradley and Robinson obtained by the interaction of diazomethane and benzoyl chloride is decomposed by iodine[12] "instantly in cold alcoholic solution with evolution of nitrogen" is clearly an error, since Wolff[11] emphasizes the fact that the reaction only takes place "in der Wärme." This is in agreement with our own observations, since we find that the decomposition of this substance begins only at 45°, being complete at 60°.

Quite a different interpretation of the reaction has been put forward by Robinson and his pupils,[13] who originally denied the production of any ω-chloro-acetophenone except "a trace detectable by the powerful lachrymatory properties and characteristic odor of this substance" when benzoyl chloride reacts with diazomethane. This trace has since been augmented by them to 9[13b] and 13%,[13c] as compared with the 72% obtained by Clibbens and Nierenstein.[3a]

According to the Robinson interpretation,[13b,c] the reaction proceeds in three stages, as follows

$$RCOCl + CH_2N_2 = RCOCHN_2 + HCl \qquad (A)$$

$$CH_2N_2 + HCl = CH_3Cl + N_2 \qquad (B)$$

$$RCOCHN_2 + HCl = RCOCH_2Cl + N_2 \qquad (C)$$

It will be realized that none of these stages accounts for the production of substances derived from Formula II. Furthermore, this interpretation assumes the formation of methyl chloride, a product identified qualitatively neither by us nor any other workers, nor even by Bradley and Robinson,[14] who state "the formation of methyl chloride . . . was not experimentally confirmed." In support of Robinson's views a series of quantitative experiments have been published by Bradley and Schwarzenbach.[15] Experiment V in their paper[16] claims that "the whole of the nitrogen and chlorine" has been "accounted for." An analysis of this experiment will thus serve best to show the inadequacy of the Robinson theory.

(1) According to the above-given equations, Reactions B and C depend on A for their HCl supply; therefore, using equimolecular quantities of benzoyl chloride and diazomethane, the *maximum* yield of methyl chloride is obviously 50%, diminishing in direct proportion as the production of $RCOCH_2Cl$ (Equation B) increases. Experiment V records, however, 57% of methyl chloride and 13% of ω-chloro-acetophenone.

(2) Assuming that the Robinson scheme is correct, and methyl chloride is produced, then clearly the nitrogen evolution expresses quantitatively the ratio of B to C. Therefore, using diazomethane corresponding to 1772 cc.

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[12] Bradley and Robinson, J. Chem Soc., 1317 (1928).

[13] (a) Bradley and Robinson, *ibid.*, 1310 (1928); (b) Bradley and Robinson, Nature, 122, 130 (1928); (c) Bradley and Schwarzenbach. J. Chem. Soc., 2904 (1928).

[14] Ref. 13a, p. 1317.

[15] Ref. 13c, pp. 2909–2912.

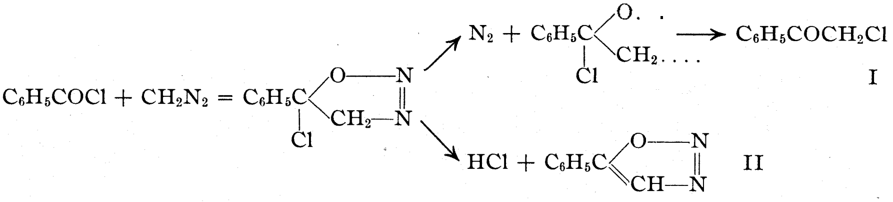
[16] Ref. 13c, p. 2911.

of N_2,[16] an evolution of 886 cc. of N_2 corresponds to a yield of 31% of ω-chloro-acetophenone and not to 13% as recorded in Experiment V.

(3) If, however, one ignores the indirect determination of methyl chloride, then the nitrogen evolution and the amount of benzoyl chloride recovered unchanged, correspond to an approximate yield of 65%, and not 13% of ω-chloro-acetophenone.

In view of these considerations, and also in view of the fact' that Experiment V is the only experiment which contains a complete analysis in support of Robinson's hypothesis, it seems to us that this hypothesis is quite unfounded, and requires further data, as well as the establishment of the production of large quantities of methyl chloride, before it can seriously be considered.

Although up to the present we have not succeeded in isolating the intermediary substance A, suggested by Lewis, Nierenstein and Rich,[3e] there is little reason to doubt that it forms the first stage in the reaction, and on decomposition subsequently leads to the production of Substances I (Schlotterbeck, Nierenstein, Arndt, Meerwein), I1 (Nierenstein), and III (Xrndt, Meerwein). In the case of the Nierenstein reaction we find that higher temperatures favor the production of Substance I since, for example, 92% of ω-chloro-acetophenone is produced at 35°, 50% at 16°, and 32% at 0°. The production of Substance IV (Arndt, Robinson), takes place to any appreciable extent at low temperatures only,[17] and the formation of Substances I and II in the case of benzoyl chloride and diazomethane is thus shown as follows



The following apparatus has been in use in this Laboratory for the last ten years, when working with diazomethane prepared according to Pechmann, in flask A, ether being added through the funnel, D, and alkali through funnel E. The diazomethane produced is slowly distilled into flask B,[18] which contains the acyl chloride dissolved in dry ether (Grig-

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[17] It must be noted that the low temperatures used by Robinson and his collaborators are a fundamental variation of the original conditions laid down by Nierenstein and his collaborators, and it is, therefore, not surprising that no concordant yields of ω-chlorinated acetophenones have been obtained by these two sets of workers. See also Nierenstein, Nature, **122,313** (1928).

[18] Flask B is manufactured in England by Messrs. Plowden and Thompson, Ltd., Stourbridge, Birmingham, who list it as the "Nierenstein flask." This flask is extensively used in these Laboratories for the recovery of ether and other volatile solvents

nard). The trap C leads into glacial acetic acid, in which manner diazomethane becomes a reagent which can safely be used without other special precautions.

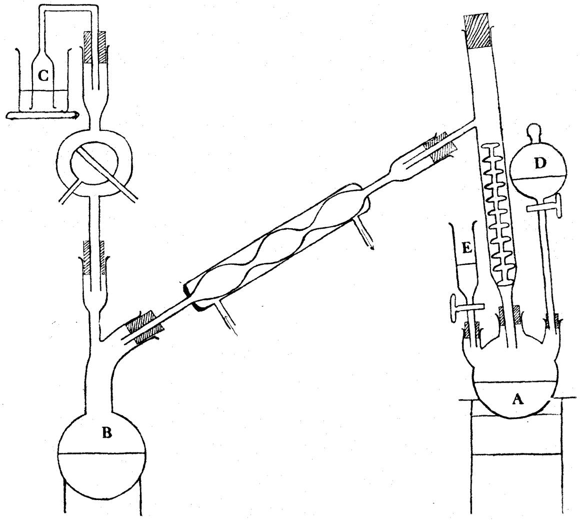

Fig. 1.

Summary

It is shown that the interaction of diazomethane with aromatic acyl chlorides proceeds on the same lines as the Schlotterbeck reaction, and requires no special interpretation, as suggested by Robinson.

BRISTOL, ENGLAND

[COMMUNICATION NO. 397 FROM THE KODAK RESEARCH LABORATORIES]

OPTICAL ROTATION OF CELLULOSIC MATERIALS. I. THE OPTICAL ROTATION OF SOLUBLE CELLULOSE IN ALKALI[1]

BY T. F. MURRAY, JR., C. J. STAUD AND H. LEB. GRAY

RECEIVED JULY 9, 1929 PUBLISHED APRIL 7, 1930

It appeared to the writers that a study of the optical rotation of the alkali-soluble portion of cellulose might help in determining the nature of the material dissolved and possibly the degradation which the cellulose has undergone.

Perhaps no reaction in cellulose chemistry has been more studied than the solubility of cellulose in alkali, almost continuously since the time of John Mercer.[2] A résumé has been published recently by G. Blanco.[3]

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[1] Presented before the Division of Cellulose Chemistry of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

[2] John Mercer, English Patent 13,296 (1850).

[3] G. Blanco, *Ind. Eng. Chem.*, 20, 926 (1928).

The optical properties of alkaline solutions of cellulose appear to have received but little attention. Hess and Messmer,[4] in 1922, determined the optical rotation of the material regenerated from cuprammonium solutions and in 1923 Hess, Weltzien and Messmer[5] gave the results of three additional observations.

Apparently the interest was to show that the material from cuprammonium solution did not give in alkali a specific rotation comparable with that in Schweizer's reagent.

Experimental

The cellulose employed was a high grade long fiber cotton known as "Eastman Filtration Cotton." It had the following analysis

or-Cellulose	98.9%[6]	Moisture	3.7%[9]
Copper number	0.064[7]	Ash	0.072%
Cuprammonium viscosity 5522 centipoises[8]			

The optical rotation was determined in a Hilger triple field polarimeter accurate to 0.01' angular rotation. The light source was a mercury vapor arc, passed through a Corning Novial glass and Didymium filter (W. and W. No. 77), giving monochromatic green light of wave length 546.1 mμ. Readings were made at 25°.

Action of Acids

Three acids were used, orthophosphoric, sulfuric and hydrochloric at concentrations of 3 N. The equivalent of 16.20 g. of dry cotton (0.10 mole of $C_6H_{10}O_5$) was immersed in 600 cc. of acid solution and allowed to stand at 54° (with occasional shaking) for twenty-four and forty-eight hours in a jacketed air-bath heated by boiling acetone.

After the acid treatment, the liquid was filtered by suction, the cellulose forming its own mat with repeated filtration. The filtrate was held for determination of its optical rotation. The residue was washed until neutral to brom thymol blue, dried at 105°, weighed to the nearest centigram and the amount dissolved in the acid thus determined.

The optical rotations of the acid filtrates were determined using 2-dm. polarimeter tubes, and the specific rotations were calculated according to the usual equation.

Two samples weighing 4.05 g. (1/40 mole of $C_6H_{10}O_5$) each of the oven dry residues from the acid hydrolysis were extracted, using with each

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[4] Hess and Messmer, *Ber.*, 55, 2436 (1922).

[5] Hess, Weltzien and Messmer, *Ann.*, 435,139 (1924).

[6] Tentative method proposed by the Cellulose Division of the American Chemical Society, *Ind. Eng. Chem., Anal. Edition, 1,* 52 (1929).

[7] Staud and Gray, *Ind. Eng. Chem.*, 17,741 (1925).

[8] Standard method proposed by the Cellulose Division of the American Chemical Society, *Ind. Eng. Chem., Anal. Edition, 1,* 49 (1929).

[9] Determined by drying for twelve hours at 105°.

TABLE I

EXPERIMENTAL RESULTS

3 *N* acid	Phosphoric		Sulfuric		Hydrochloric	
Treatment, hours	24	48	24	48	24	48
Loss of wt., g.	0 06	0	0 11	0 20	0 42	0.73
°α	0 0	. .	+0 02	+0.03	$0 05	+0 08
$[\alpha]$	0.0	. .	+54 5	+45 0	+35.7	$33.0

sample 40.5 cc. of 17.5% sodium hydroxide (grams per 100 g. of solution) for twenty-four hours at room temperature, 23–25' with occasional agitation. The material was then filtered by suction on a tared Gooch crucible, the cellulose forming its own mat with repeated filtration. The filtrate was held for polarimetric examination and the residue washed as in the a-cellulose determination.[6] This method was used for the sulfuric and phosphoric acid treated materials.

The hydrochloric acid product was too highly degraded to use the above method. It was separated by centrifuging and washed in the cups with water, 10% acetic acid, and again with water until neutral to litmus. The material was then dehydrated by 95% alcohol and finally ether.

All residues were dried at 105° and weighed. The weight differences were used in calculating the specific rotations. The amounts of material dissolved and the rotations of the alkaline extracts are given in Table II. The alkali extract of the sample hydrolyzed for twenty-four hours with hydrochloric acid was too hazy to read as obtained. It was diluted with two volumes of 17.5% sodium hydroxide and the rotation multiplied by three.

TABLE II

EXPERIMENTAL DATA

Acid used for hydrolysis	Time of acid treatment, hours	Material extracted by 40 5 cc. of 17 5% NaOH, g	Dissolved in 17 5% NaOH, %	Length of tube, dm	α	$[\alpha]$
	24	0 13	3 2	2	–0 08°	–12 5°
	24	10	2 5	2	– 08°	–16 2°
				0 5	– 02°	–16 2°
	48	12	3 0	2	– 08°	–13 5°
				0 5	– 03°	–20 2°
	48	11	2 7	2	– 08°	–14 7°
				0 5	– 02°	–14 7°
H_2SO_4	24	30	7 4	2	– .14°	– 9 5°
	24	.25	6 2	2	– 14°	–11 4°
	48	42	10 4	2	– 25°	– 9 1°
	48	42	10 4	0 5	– 05°	– 7 3°
HCl	24	1 37	33 8	0 5	– 21°	–12 4°
	24			0.5	– 18°	. .
	48			0 5	– 21"	
	48	1 94	48 0	0 5	– 23°	– 9 6°

Action of Oxidants

Potassium permanganate and potassium dichromate were used as oxidants. All oxidations were conducted in *N* orthophosphoric acid. Concentrations of 0.5 and 2 available oxygen atoms per unit of $C_6H_{10}O_5$ were used. Oxidations were at room temperature, 23–25" and at 54° for two and six hours at each temperature.

As a control phosphoric acid was used alone under the same conditions, the product being filtered by suction, washed until neutral to brom thymol blue and dried at 105°. The differences in weights between the untreated material and the phosphoric acid products varied from 0.01 to 0.08 gram, which was disregarded since the maximum loss is less than $^1/_2$%.

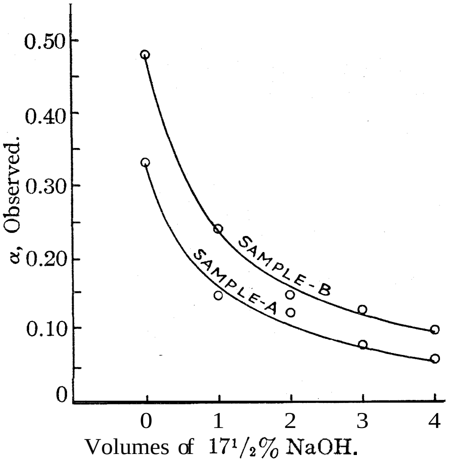


Fig. 1.—Relation between optical rotation and dilution of alkaline extracts of oxidized cellulose.

In all oxidations the equivalent of 16.20 g. of oven-dried cellulose was used; 600 cc. of oxidizing solutions were prepared by dissolving 3.2 g. and 12.7 g. of potassium permanganate, and 9.8 g. and 39.2 g. of potassium dichromate, respectively, in 600 cc. portions of *N* phosphoric acid. In runs at 54° the cotton and solution were each heated to that temperature before mixing.

The products from potassium dichromate were filtered with suction and washed with water. The residual dichromate was removed as indicated by lead acetate and dried at 105°. The loss in weight was from 0.01 to 0.06 g., or less than 0.4%.

The products from potassium permanganate were filtered by suction, except those oxidized at the higher concentration, which were separated by centrifuging. The excess permanganate, if any, was removed by wash-

TABLE III

LOSS IN WEIGHT OF CELLULOSE DUE TO OXIDATION WITH POTASSIUM PERMANGANATE

Available oxygen atoms per $C_6H_{10}O_5$	Time of oxidation, hours	Temp., °C.	Loss in weight, g.	Loss, %
0.5	2	23	0.09	0.56
0.5	6	23	0.13	0.80
2	2	23	0.28	1.7
2	6	23	1.38	8.5
0.5	2	54	0.72	4.5
0.5	6	54	0.93	5.7
2	2	54	4.01	24.8
2	6	54	4.11	25.4

ing with water and the manganese dioxide dissolved using dilute sodium bisulfite containing a little hydrochloric acid. The product was washed with water until neutral to brom thymol blue and dried at 105°. The losses in weight are given in Table III.

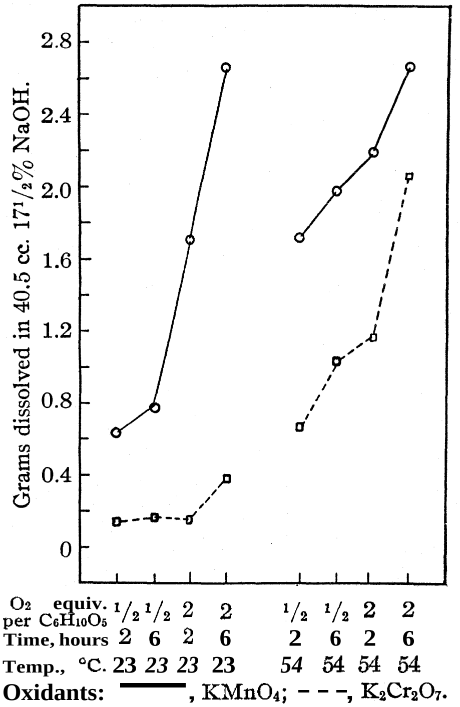


Fig. 2.—Relation between oxidizing conditions and weight dissolved in 17.5% NaOH.

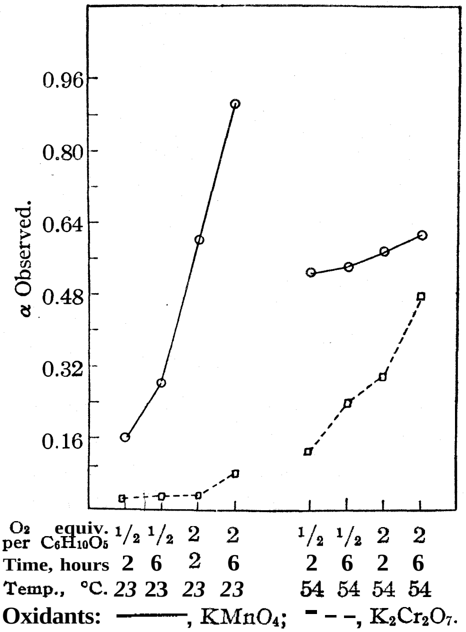
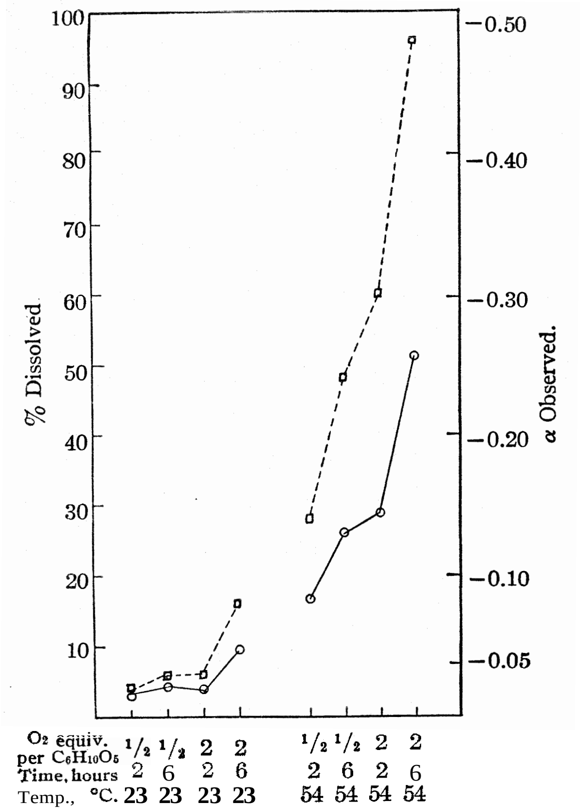


Fig. 3.—Relation between oxidizing conditions and the observed rotation of the alkaline extracts.

When the cellulose was treated at 54° with 0.5 and 2 oxygen equivalents for six hours, the color of the potassium permanganate had entirely disappeared after approximately three hours, but manganese dioxide was present even at the close of the six-hour period.

The filtrates from the solutions with two oxygen equivalents of permanganate in the two and six hour treatments at 54°, after decolorizing by the addition of a minute quantity of sodium bisulfite crystals, were read. The two-hour sample showed no optical activity and the six gave −0.03° in a 2-dm. tube, corresponding to a specific rotation of about −2°.



——, % Dissolved in 17½% NaOH; – – –, observed rotation.

Fig. 4.—Oxidation with potassium dichromate. Effect of conditions on amount dissolved in alkali and observed rotation.

Four and five-hundredths grams ($^1/_{40}$ mole of $C_6H_{10}O_5$) of each of the oxidized materials were extracted for twenty-four hours at room temperature, 23–25°, with 40.5 cc. of 17.5% sodium hydroxide, treated as described under the alkaline extraction of hydrocellulose, filtered where practicable and centrifuged when necessary.

TABLE IV

EXPERIMENTAL RESULTS

Oxidant	Available oxygen atoms per $C_6H_{10}O_5$	Time of treatment hours	Temp., °C.	Grams dissolved in 17.5% NaOH	Dissolved in 17.5% NaOH	a	[α]	Dilution, volumes of 17.5% NaOH added
$KMnO_4$	0.5	2	23	0.58	14.3	−0.14	−19.6	1
				0.69	17.0	− .18	−21.1	2
	0.5	6	23	0.75	18.5	− .28	−30.4	1
				0.80	19.8	− .28	−28.4	2
	2	2	23	1.53	37.8	− .60	−31.8	0
				1.89	46.6	− .51	−21.9	2
	2	6	23	2.66	65.8	− .90		2
						− .90	−27.4	4
	0.5	2	54	1.72	42.5	− .51	−21.3	2
						− .54		2
	0.5	6	54	1.98	49.0	− .54		2
						− .54	−22.2	2
	2	2	54	2.19	54.1	− .63	−23.4	2
						− .51		2
	2	6	54	2.67	66.0	− .57		2
						− .65	−17.3	4
$K_2Cr_2O_7$	0.5	2	23	0.14	3.5	− .02	−11.6	0
						− .01		0
	0.5	6	23	0.17	4.2	− .03	−14.3	0
						− .02		0
	2	2	23	0.15	3.7	− .03	−16.2	0
						− .03		0
	2	6	23	0.39	9.4	− .08	−16.6	0
						− .07		0
	0.5	2	54	0.67	16.5	− .15	−17.9	0
						− .12		2
	0.5	6	54	1.04	25.7	− .24	−18.7	2
						− .24		2
	2	2	54	1.17	28.9	− .27	−18.7	2
						− .33		2
	2	6	54	2.14	52.9	− .45	−17.0	2
				1.99	49.1	− .51	−20.7	2
Controls, H_3PO_4, no oxidant, original cotton	...	2	23	0.09	2.2	− .01	− 9.0	0
	...	6	23	0.08	2.0	− .02	−20.4	0
	...	2	54	0.07	1.7	− .02	−23.2	0
	...	6	54	0.06	1.5	− .02	−27.0	0
	...		..	0.09	2.2	− .02	−18.0	0

TABLE V

OPTICAL ROTATION OF DILUTED ALKALINE EXTRACTS

Volumes of 17.5% NaOH added	Sample A Obs. a	Sample A Calcd. a	Sample B Obs. a	Sample B Calcd. a
0	−0.33	a −0.33	−0.48	a −0.48
1	− .15	2α − .30	− .24	2a − .48
2	− .12	3α − .36	− .15	3α − .45
3	− .08	4α − .32	− .13	4α − .52
4	− .06	5α − .30	− .10	5α − .50

The alkaline extracts were read and the results are given in Table IV. When too dark in color or too hazy the solutions were diluted with 17.5% sodium hydroxide. The dilutions are indicated in the table and the values under α are equal to the observed rotation multiplied by [1 + (the dilution factor)].

The validity of diluting with 17.5% sodium hydroxide was established as follows. Two samples of cellulose of high alkali solubility were extracted and clear initial solutions obtained. Portions were diluted with 0, 1, 2, 3 and 4 volumes of 17.5% alkali and readings made. The results are given in Table V and shown graphically in Pig. 1.

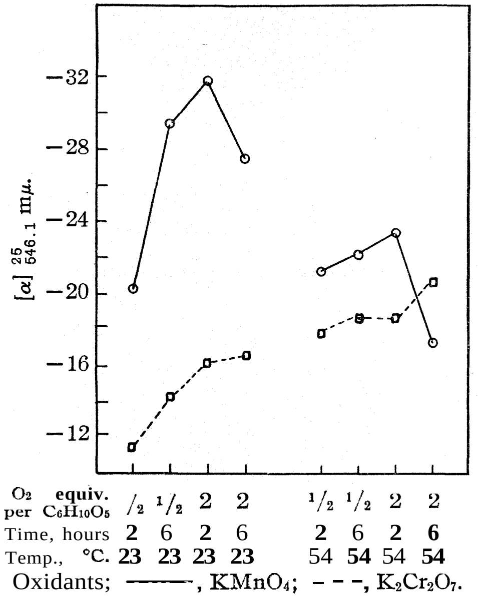


Fig. 5.—Effect of oxidizing conditions on the apparent specific rotation of the alkaline extracts.

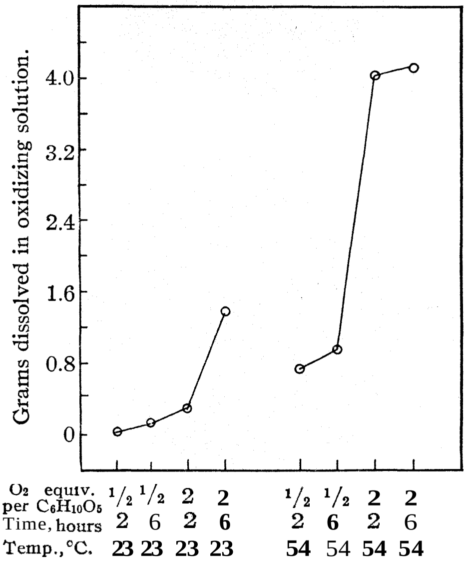


Fig. 6.—Relation between oxidizing conditions using $KMnO_4$ and weight dissolved in oxidizing solution.

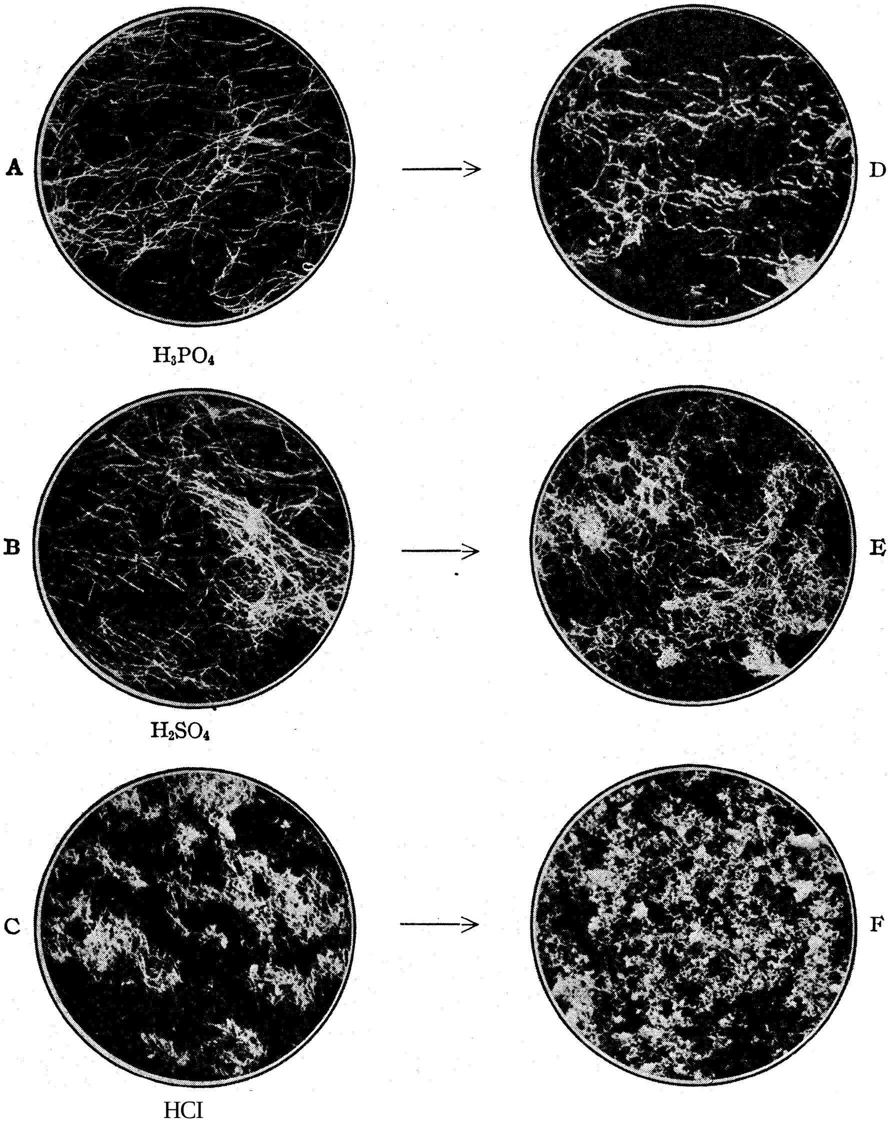
Discussion of Results

Action of Acids.—The activity of the acid solutions, indicated by material dissolved and fiber breakdown (Plate I, A, B and C) increased in the order orthophosphoric, sulfuric and hydrochloric acids.

The acid filtrates were all dextrorotatory, indicating possibly dextrose. Dextrose in the three 3 N acids gave specific rotations of +61.0°, +61.0° and +62.0°. The small amounts dissolved during acid hydrolysis render the specific rotations somewhat doubtful.

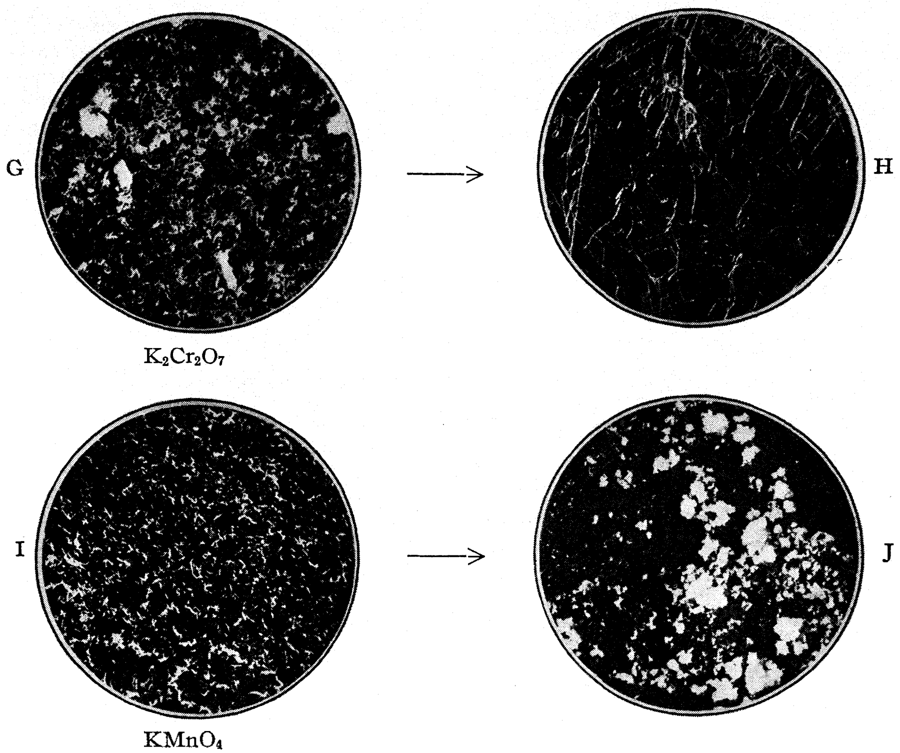
The alkaline extracts varied from 2.5% for the phosphoric to 48% for the hydrochloric acid hydrocellulose (Table II). All were levorotatory (from −0.02 to −0.23°), confirming the observations of Hess[4,5] and his co-workers on regenerated cellulose.

Action of Oxidants.—The loss in weight by potassium dichromate oxidation varied from 0.06 to 0.37% [approximating the N phosphoric



The effect of 3 N acids at 54° for forty-eight hours on cellulose.

The effect of 17½% sodium hydroxide on the corresponding hydrocelluloses.



The effect of oxidants on cellulose using 2 oxygen equivalents per $C_6H_{10}O_5$ for six hours at 54".

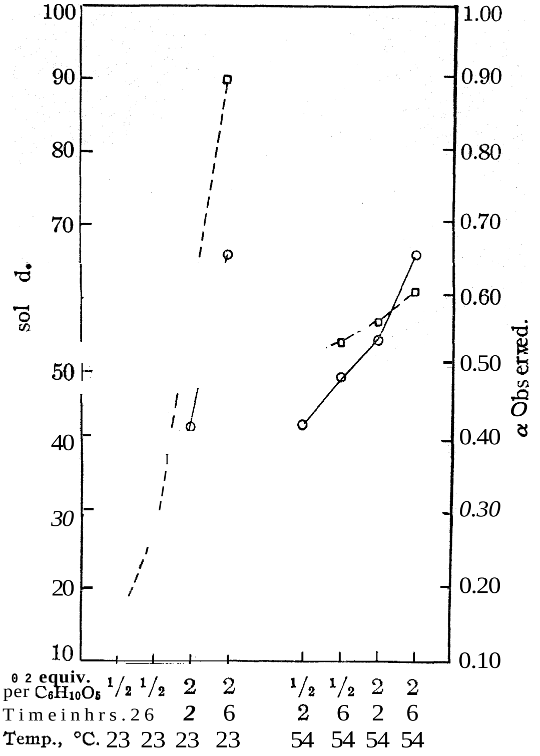
The effect of 17½% sodium hydroxide on the corresponding oxidized celluloses.

Plate II.

acid control. The 17.5% sodium hydroxide soluble was 0.14 to 2.14 g. (Fig. 2 and Table IV), increasing steadily for that treated at 54°. All observed rotations were levorotatory (from –0.02 to –0.48°, Fig. 3). The apparent specific rotations were –11.6' to –20.7' (Table IV and Fig. 5). Both the observed and specific rotations increase with more severe oxidation. A parallelism between weight dissolved and observed rotations appears to exist (Fig. 4).

With potassium permanganate from 0.56 to 25.4% dissolved (Table III and Fig. 6), which is a marked difference from the potassium dichromate oxidation. Alkaline extracts contained from 0.58 to 2.67 g. (Table IV and Fig. 2). These values fall into two groups, depending upon the temperature of oxidation, each increasing with increased severity of oxidation. The parallelism of the potassium dichromate series (Fig. 4) is not as marked in this case (Fig. 7). Apparent specific rotations of the alkaline extracts pass through maxima at both temperatures (Fig. 5).

The term "apparent" specific rotation has been used because probably more than one substance is present in the alkaline solution, and the concentrations are based on weight differences. It is assumed that no volatile products were lost.



———, % Dissolved in 17½% NaOH; – – –, observed rotation.

Fig. 7.—Oxidation with potassium permanganate. Effect of oxidizing conditions on amounts dissolved in alkali and observed rotation.

Acknowledgment.—The authors wish to express their gratitude to Mr. A. A. Robson for the preparation of the photomicrographs appearing in this paper.

Summary

1. Hydrocelluloses have been prepared by the action of phosphoric, sulfuric and hydrochloric acids and the specific rotations of the acid filtrates determined.

2. The hydrocelluloses have been extracted with 17.5% of sodium hydroxide and the specific rotations determined.

3. Long fiber cotton has been oxidized with potassium dichromate and potassium permanganate, extracted with 17.5% sodium hydroxide and the optical rotations have been determined.

4. Photomicrographs showing fiber breakdown are given.

Organic Research Laboratory
Eastman Kodak Company
Rochester, New York

[Contribution from the Research Laboratory of Organic Chemistry, Massachusetts Institute of Technology, No. 48]

THE ALIPHATIC DIOLEFINS. III. THE BEHAVIOR OF Δ-1,5-HEXADIENE AND Δ-2,4-HEXADIENE TOWARD HYDROCHLORIC ACID

By Frank Cortese[1]

Received July 19, 1929 Published April 7, 1930

In a previous paper from this Laboratory,[2] it was shown that Δ-1,5-hexadiene, when treated with sulfuric acid, gives either esters of hexanediol-2,5 and its internal ether, or polymers, according to the temperature and acid concentration employed. It was shown, further, that the polymers are not formed from the hydrocarbon, but are condensation products of the internal ether. The behavior of this hydrocarbon toward hydrochloric acid is analogous. Mainly a mixture of 5-chloro-1-hexene and 2,5-dichlorohexanes is formed, together with some diallyl oxide and a trace of its condensation products. On the other hand, the conjugated isomer, Δ-2,4-hexadiene, gives a mixture of monochlorohexenes and polymers. No dichlorohexanes are obtained.

Experimental Work

The Action of Hydrochloric Acid on **Δ-1,5-Hexadiene.**—Wurtz[3] obtained a mixture of 5-chloro-1-hexene, boiling at 130–140°, and 2,5-dichlorohexane, boiling at 170–180°, when he treated Δ-1,5-hexadiene with concentrated hydrochloric acid in sealed tubes. Both were analyzed for chlorine.

In our work 100 cc. of diallyl was shaken with 500 cc. of concentrated hydrochloric acid for 120 hours. A deep green layer of 96 cc. resulted. It was washed with 15%

Table I

Constants Obtained for the Compounds

	5-Chloro-1-hexene		2,5-Dichlorohexane	
Boiling point, °C. (mm.)	28–30 (13) 64–66 (103)	43–45 (45) 121–125 (760)	56–58 (9) 104–106 (84)	85–87 (38) 176–178 (760)
Density, d_4	$0.9141^{20°}$	$0.8891^{25°}$	$1.0686^{0°}$	$1.0441^{25°}$
Index of refr., n_D	$1.4332^{15°}$	$1.4305^{20°}$ $1.4279^{25°}$	$1.4487^{15°}$	$1.4465^{25°}$
Molecular refr.	Calcd. 34.34	Found 34.31	Calcd. 39.32	Found 39.64

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[1] Research Associate, Massachusetts Institute of Technology, 1926–1928.

[2] Cortese, *Ber.*, 62, 504 (1929).

[3] Wurtz, *Ann. chim. phys.*, [4] **3**, 155 (1864).

sodium chloride, 5% sodium hydroxide, again with 15% sodium chloride, dried over calcium chloride and fractionally distilled. The yield of combined chloro compounds was found to be 80%, 57% being the dichloro and 23% the monochloro. The rest of the yield could be accounted for as diallyl oxide with a small amount of its polymeric condensation products.

Meso-2,5-dichlorohexane.—As our product of 2,5-dichlorohexane was evidently a mixture of stereoisomers, it was desirable to isolate the two forms. This was done by chilling to −50° and separating the crystals which deposited from the mother liquor by means of the centrifugal filtration device of E. L. Skau.[4] The solid form obtained was presumably the meso form, thus isolated for the first time. It was recrystallized from pentane and distilled. Constants of the meso form: b. p. 177.8–178.2° (corr. at 751.8 mm.); f. p. (by cooling curve) 18.7"; m. p. (by heating curve) 18.7"; d_4^{25} 1.0459.

The liquid residue (mother liquor from the meso crystalline form) now presumably enriched in the racemic form was distilled and a fraction obtained having a boiling range of one degree. That it had a slightly higher boiling point and lower density than the original mixture is shown by the data given—liquid residue: b. p. 176.4–177.4° (corr. at 751.1 mm.); d_4^{25} 1.0431; d_4^0 1.0675.

Behavior of Δ-2,4-Hexadiene toward Hydrochloric Acid

I. Toward Concentrated Aqueous Acid.—Fifty cc. of hydrocarbon was shaken with 250 cc. of concentrated acid for twenty hours. The 50-cc. dark violet layer was washed with 10% sodium hydroxide, 15% sodium chloride, shaken with calcium chloride and dried over pearl ash. It was separated into three portions by fractionation.

(1). 13 g.: b. p. 21–25' at 6.5 mm.; colorless, mild rancid odor; turns yellow on standing. B. p. 122–126° at 760 mm.; d_4^0 0.9111; d_4^{25} 0.8865; n_D^{15} 1.4417; n_D^{25} 1.4360. It titrated for one double bond. Molecular refraction found, 34.92; calculated, 34.31. It was evidently a mixture of monochlorohexenes.

(2). 10 g.: b. p. 81–84' at 4.5 mm.; light yellow; faint parsley odor; deeper yellow on standing. B. p. 213–223° at 760 mm. Distillate intense violet, fumes with hydrogen chloride and has strong odor of parsley. (Vacuum distilled sample): d_4^0 0.9002; d_4^{25} 0.8801; n_D^{24} 1.4670. Titrated for one double bond, if assumed to be the dimer. *Anal.* (Parrbomb.). Calcd. for dichlorohexanes: Cl, 45.8 and for dimer monochloride $(C_6H_{10})_2HCl{:}Cl$, 17.7. Found: Cl, 15.7.

Shaking with excess standard sodium hydroxide and titrating the unused alkali with standard acid, using phenolphthalein as the indicator, showed that the chlorine content is practically all hydrolyzable in the cold by $N/10$ sodium hydroxide.

Both density and boiling point exclude the possibility of dichlorohexanes. This fraction probably consists of a mixture largely of dimer monochloride, some dimer and a little free hydrochloric acid.

(3). Tar residue.

II. Toward Alcoholic Hydrochloric Acid.—Five cc. of Δ-2,4-hexadiene was dissolved in 50 cc. of 95% alcohol saturated with hydrochloric acid gas. The opalescent solution very soon developed a pink color. In one hour it was deep violet with colorless oil drops settling out. In three hours it was opaque deep purple with more oil drops. After one week it was deep purple-red, but the odor of unchanged hydrocarbon was very strong. It was diluted with water, which changed the color to light yellow. The yellow oil was washed with water, dried with pearl ash and distilled. It was found that only two-fifths of the hydrocarbon had been attacked; one-half of this was ac-

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[4] For a description of this device, together with its use in separating the meso-2,5-dichlorohexane described here, see Skau, *J. Phys. Chem.*, 33,951 (1929).

counted for as the monochlorohexenes and one-half as polymeric products. The violet colors always observed are due to the action of the acid on the polymers formed.[5]

Summary

1. Hydrochloric acid reacts with Δ-1,5-hexadiene to give a mixture of 5-chloro-1-hexene, 2,5-dichlorohexanes, diallyl oxide and a trace of its condensation products.
2. From the 2,5-dichlorohexane the meso form was separated as pure crystals.
3. Hydrochloric acid reacts with Δ-2,4-hexadiene to give *a* mixture of monochlorohexanes and polymeric products of the hydrocarbon.

MUNICH, GERMANY

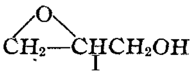
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

STUDIES OF GLYCIDOL. I. PREPARATION FROM GLYCEROL MONOCHLOROHYDRIN[1]

BY T. H. RIDER AND A. J. HILL

RECEIVED JULY 24, 1929 PUBLISHED APRIL 7, 1930

The usefulness of ethylene oxide in synthetic work has been demonstrated in convincing fashion during the past few years, and for this reason a peculiarly attractive field of investigation is offered by a study of the closely related glycidol, I (epihydrin alcohol). This compound has not been readily available, nor have its chemical properties been adequately studied. Its synthesis has therefore been carefully investigated by the writers with a view to an extensive study of its addition reactions.


I

We have found that any practicable method of synthesis must needs use glycerol monochlorohydrin as the starting material. While both the alpha and beta-isomers of monochlorohydrin are converted into glycidol by the removal of hydrogen chloride, it is of considerable academic importance to know whether or not both isomers are formed in a given reaction used for the preparation of one or the other. There have been no simple tests which would differentiate the two compounds and no solid derivatives of the isomeric monochlorohydrins have been sufficiently described in the literature to make their preparation a safe criterion of structure. In the course of the present investigation the presence of the two isomers in a chlorohydrin mixture has been determined by a qualitative method, which depends upon the fact that the phenylurethans of the isomeric compounds are decidedly different in their properties. The phenylurethan of the alpha-isomer

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[5] Cf. McCullough and Cortese, THIS JOURNAL, 51,225 (1929).

[1] Constructed from part of the thesis presented by T. H. Rider to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy, 1928.

melts at 129°, while that of the beta-isomer melts at 133°. Mixtures of the two melt from 115–121°. Furthermore, the two compounds show decidedly different crystal structures.

The Preparation of Glycerol α-Monochlorohydrin.—Either gaseous hydrogen chloride or aqueous hydrochloric acid may be used in the direct synthesis of glycerol monochlorohydrin from glycerol. The yields previously reported in the literature have never exceeded 70% with the exception of certain patent claims which appear to be quite inaccurate.

As the result of preliminary work we regarded the reaction using aqueous hydrochloric acid as being the most practical. Even in this method, however, the maximum yield of monochlorohydrin can be obtained from a single run only with the concomitant production of an undesirably large amount of dichlorohydrin. To overcome this waste of glycerol, we have developed a new procedure for the reaction between glycerol and aqueous hydrochloric acid, catalyzed by acetic acid. The conditions are so regulated as to give a maximum formation of monochlorohydrin with a minimum of the dihalogenated product. After isolation of the monochlorohydrin, the rather large glycerol-containing residue is used again. It is desirable to combine the residues from two such reactions and use this mixture as raw material for a third. (Note.—Mixing the residue from one reaction with fresh glycerol for the next leads to a rapid accumulation of polyglycerides.) By following closely a set of conditions which was evolved from an extensive study of many factors, yields of 85–88% may consistently be obtained.

The Preparation of Glycidol.—It has been stated above that syntheses of glycidol from intermediates[2] other than monochlorohydrin are in general impracticable. Of these less desirable reactions, mention might be made of Breslauer's method which utilizes epichlorohydrin, but which gives poor yields and a product of doubtful purity.

A number of reagents may be used, with more or less success, to remove hydrogen chloride from monochlorohydrin. Nef[2] has reported 70% yields of glycidol by the use of alcoholic potassium hydroxide. The procedure of Nef calls for the mixing of solutions of monochlorohydrin and potassium hydroxide in 95% alcohol at room temperature, filtering off the precipitated salt after fourteen hours, and separating the alcohol and glycidol by distillation.

A study of the reaction has shown that this yield can be obtained only when several changes are made in Nef's procedure. Absolute alcohol, rather than 95%, should be used; the reactants should be thoroughly

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[2] Grün, *Ber.*, *59*, 690 (1926); Prileschauew, *ibid.*, 42, 4811 (1909); Nef, *Ann.*, 335, 1 (1904); Jowanowitsch, *Monatsh.*, **6**, 467 (1885); Richter, *Ber.*, 10, 697 (1877); Gegerfelt, Bull. *soc. chim.*, [1] 23, 160 (1875); Laufer, *Jenaer. Zeitschrift*, 10, **2**, Spl. S. 141; Breslauer, J. *prakt. Chem*., 20, 188 (1879).

cooled before mixing; the glycidol should be isolated within thirty minutes, and the solvent alcohol removed under diminished pressure. Distillation at atmospheric pressure is attended with the formation of a considerable quantity of glycerol monoethyl ether. By the use of this modified procedure a crude yield of 79% can be obtained.

Unfortunately the great solubility of glycidol in alcohol is a factor which militates against the success of this method. It is impossible to obtain a sharp fractionation of the reaction mixture under reduced pressure and consequently, in order to secure a product free from alcohol, a large amount of glycidol is lost in the solvent fraction. Thus the yield of 79% is reduced to 64% upon further distillation, and the product retains some alcohol.

Since the absence of water from the reaction mixture is desirable from theoretical considerations, an alcoholic solution of sodium ethylate was used in place of the alcoholic potash solution. The yields were higher, and glycidol of a reasonable degree of purity was obtained in amounts 65–68% of the theoretical.

The use of alcohol as a solvent is undesirable, first, because it conduces always to the formation of glycerol monoethyl ether and, second, because it is impossible to isolate all of the glycidol from the alcoholic solution. We have studied the action of solid potassium hydroxide and also solid sodium ethylate on ethereal solutions of monochlorohydrin. When solid potash in the form of a fine powder is stirred with an ethereal solution of monochlorohydrin, a water layer is formed. We have found that in the partition of glycidol between water and ether, there is very little glycidol in the ether layer, consequently in this reaction there is a concentration of the product in the water layer. Since this solution is strongly alkaline it produces a comparatively large amount of hydrolysis, and the yield of glycidol is reduced to 50% of the theoretical.

While the action of solid pulverized sodium ethylate[3] on ethereal solutions of monochlorohydrin does not produce a second liquid phase, the yields are lower than with the solid potash. Since the yields are likewise lower than in the reaction using an alcoholic solution of sodium ethylate, it must be assumed that there is a relatively large amount of direct replacement of halogen by the ethoxy radical. This hypothesis was substantiated by the isolation of rather large amounts of glycerol ethyl ether from the products of reaction, more indeed than was found in the case of a carefully controlled reaction run in alcohol solution.

The presence of both water and alcohol in the reaction mixture may be obviated by reacting metallic sodium with an ethereal solution of monochlorohydrin. This reaction has been studied to a limited extent by Reboul,[4]

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[3] A method, similar in principle, utilizes monosodium glycerate, cf. Nivière, Compt. rend., 156, 1628 (1913). We have obtained 25–27% yields by this procedure.

[4] Reboul, Ann. *chim.*, **[3]** ***60*, 1** (1860).

Bigot[6] and Nivière.[6] The last mentioned claims yields of 55%, while the other investigators state that the yields are low. The yield given by Nivière, and obtained by reacting equimolecular proportions of sodium and monochlorohydrin, could not be duplicated by the writers. When the reaction was continued until the sodium was completely reacted, the precipitate of salt, originally granular, became extremely pasty, and the reaction was increasingly slow, it being almost impossible to cause the last pieces to react. The pasty nature of the precipitate was due to the formation of ether-insoluble polymerization products. By stopping the reaction before the sodium was completely reacted, the salt precipitate remained granular and the yields of glycidol were much higher. For this reason a series of reactions was carried out in which different amounts of sodium were used. The results of these reactions are shown in the accompanying graph, in which the moles of sodium reacting with one mole of monochlorohydrin are plotted against the yield calculated from the latter.

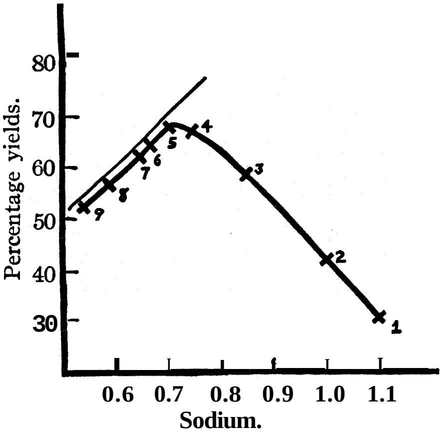

Fig. 1.

The thin diagonal line represents the limiting yields with the amount of sodium used. Thus it is clearly seen that sodium plays two roles, the first to produce glycidol, and the second to destroy it. There are two factors by the control of which the rate of destruction may be made negligible when compared to the rate of formation. The first of these, the mass action factor, entails the use of a reduced amount of sodium. Not only must the total quantity be less than the theoretical, but the sodium should be used in the form of a fine wire, so that the reaction will proceed with reasonable rapidity. The second factor is the temperature at which the reaction is carried out. The optimum temperature is 10–15°. Below 0° the formation proceeds so slowly that it is not practicable to use this temperature. Above 25° the rate of formation is increased, but the rate of destruction becomes correspondingly greater, so that no glycidol can be isolated from the reaction mixture.

With the method of preparation finally adopted, there is considerable monochlorohydrin in excess over the amount of sodium. After removal of the solvent and the distillation of the glycidol from the reaction mixture, an average of one-quarter of a mole of monochlorohydrin may be recovered.

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[5] Bigot, Ann. *chim.*, [6] 22, 433 (1891).

[6] Nivière, *Bull. soc. chim.*, 15, 464 (1914).

Redistilled glycidol is obtained in yields of 90% calculated from the chlorohydrin actually used. Not only is this yield a great improvement over those previously reported, but the reaction product is obtained in a high degree of purity. Indeed, the impurity of the glycidol resulting from some procedures has led to erroneous statements in the literature concerning its chemical and physical properties.

Glycidol may be conveniently identified by means of its phenyl- and α-naphthylurethans. The former melts at 60° and the latter at 102°.

Experimental Part

The Phenylurethans of the Isomeric Glycerol Monochlorohydrins.—Phenyl isocyanate is stirred with a slight excess of chlorohydrin, or a mixture of isomeric chlorohydrins. When the reactants form a homogeneous solution the mixture is heated on a steam-bath until there is no longer an obvious odor of phenyl isocyanate. The reaction mixture is dissolved in a rather large volume of acetone and water added until the solution is cloudy. If enough water has been added to throw out an oil, the whole colloidal solution is filtered on a coarse folded filter paper, which retains the oil. This filtered colloidal solution, on standing, separates a flocculent solid, which is filtered off and recrystallized from high-boiling petroleum ether. When the urethan has been prepared from a mixture[7] of the isomeric a- and β-glycerol monochlorohydrins, the isomeric urethans may be separated by fractional crystallization from a solvent consisting of a mixture of acetone and high-boiling petroleum ether. More convenient, however, is another method of separation. The mixed urethans, if allowed to crystallize slowly from a solution in high-boiling petroleum ether, separate in different forms. The P-urethan deposits first, in dense clusters, which adhere to the sides of the flask, while the α-isomer precipitates in a flocculent form, which will, for the most part, remain suspended in the solvent so that a decantation will effect a good separation. By repeating this procedure the two forms may be separated completely, as evidenced by microscopic examination. The phenylurethan of a-monochlorohydrin melts at 128–129° and remelts at 129°. The phenylurethan of p-monochlorohydrin melts at 131–133° and remelts at 133°.

Anal. Calcd. for $C_{10}H_{12}O_2NCl$: N, 6.10; Cl, 15.5. Found: α-urethan—N, 6.14, 6.15; Cl, 15.0, 15.2. β-urethan—N, 6.2; Cl, 15.6.

Glycerol α-Monochlorohydrin.—Glycerol is mixed with three and three-quarters parts by weight of concentrated hydrochloric acid (sp. gr. 1.19) and one-tenth part by weight of glacial acetic acid. The mixture is heated on a steam-bath for a period of ten hours, after which it is distilled. The water fraction is removed under the vacuum produced by a water pump (10–15 mm.), during heating by steam. The fractionation is automatic and heating is continued as long as there is a distillate. The residue is now distilled, preferably through a short column. The chlorohydrin is collected from 117–130° at 15 mm. (100–112° at 3–5 mm., or about 81° at 0.5 mm.) and the residue saved. Provided the first distillation has been carried to completion, in the second distillation the temperature should rise rapidly to the boiling point of the chlorohydrin, so that there is no need for a further cut of low-boiling material. The residues from two such reactions are combined and hydrochloric and acetic acids added in the same proportions by weight that were mixed with glycerin in the original preparations. This reaction mixture is heated for a period of fourteen or fifteen hours instead of ten. The distillations are carried out in the same manner. The combined yields from the two original runs

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[7] Such as that derived from the action of hypochlorous acid on allyl alcohol.

and the re-working of the residues is 85–88%, and the density of the once distilled material is 1.317.

Anal. Calcd. for $C_3H_7O_2Cl$: Cl, 32.09. Found: Cl, on crude product, 27.40 to 32.21; Cl, on redistilled material, 32.10, 32.07.

Purified monochlorohydrin, prepared according to the new procedure, has d^{25} 1.3217; n_D^{25} 1.4811; it remains liquid at −17°, and freezes to a glass in liquid air. It is miscible in all proportions with ether, water, alcohol and acetone. It is soluble in hot benzene and very slightly soluble in cold benzene, petroleum ether, xylene, heptane, diphenylmethane and diphenyl ether. When distilled at a pressure of 0.53 mm., the temperature of distillation is 80.9°.

Glycidol. (a) By the Action of Alcoholic Potassium Hydroxide on **Monochlorohydrin.**—One mole of potassium hydroxide is dissolved in 400 cc. of absolute alcohol and the solution cooled in an ice-bath. A cold solution of one mole of glycerol a-monochlorohydrin in 200 cc. of absolute alcohol is added during stirring. The reaction mixture is allowed to stand for twenty to thirty minutes, after which it is filtered. The alcohol is removed under reduced pressure and the glycidol distilled from the residue. The first collection is made from 60–100° at a pressure of approximately 10 mm. It is necessary to redistil this product at least twice to remove the alcohol completely, the final collection being made from 65–66°, at a pressure of 2–2.5 mm. The yield of redistilled glycidol is about 60%. The preparation of solid urethans for characterization purposes is given below.

(b) By the Action of Alcoholic Sodium **Ethylate** on **Monochlorohydrin.**—One mole of metallic sodium is dissolved in 400 cc. of absolute alcohol and the solution cooled in an ice-bath. A cold solution of one mole of glycerol α-monochlorohydrin in 200 cc. of absolute alcohol is added during stirring. The resulting solution is allowed to stand for about an hour, when it should be neutral, and the precipitate coagulated. The solution is then filtered and the alcohol removed under reduced pressure. The glycidol is then distilled as described in the previous reaction. The yield of redistilled glycidol is 65–68% of the theoretical. The purity was determined by the preparation of the phenyl- and a-naphthylurethans.

(c) By the Action of Metallic Sodium on **Monochlorohydrin.**—One mole of glycerol monochlorohydrin is dissolved in 600–800 cc. of strictly anhydrous ether. This solution is placed in a three-necked round-bottomed flask equipped with a mechanical stirrer through the central neck. One of the side necks is equipped with a baffle to make the stirring more effective. The flask is placed in a bath of running cold water at 10–12°. A maximum of seven-tenths of a mole of metallic sodium in the form of a fine wire is now introduced so that it winds around the stirrer and is thus swept through the solution, keeping the surface clean. The solution is stirred vigorously until the sodium is entirely reacted (from six to eight hours). The salt is then filtered off and thoroughly washed with fresh anhydrous ether. The ether is removed and the glycidol distilled as previously described. One redistillation gives a product of high purity, in yields of 95% calculated from the amount of sodium used. After distillation of the glycidol from the reaction mixture, a large amount of unused monochlorohydrin may be recovered by further distillation of the residue. The yield of glycidol, calculated from the weight of monochlorohydrin actually used—that is, the difference between the weight added and that recovered—is about 90% of redistilled material, boiling over a range of one to two degrees.

Anal. Calcd. for $C_3H_6O_2$: C, 48.62; H, 8.17. Found: C, 48.66; H, 8.13.

Glycidol is soluble in ether, alcohol, water, acetone, chloroform and benzene; it is but slightly soluble in petroleum ether and xylene. At a pressure of 2–2.5 mm. it distils at 65–66°, and at a pressure of 1 mm., using an oil-bath at 72°, it distils at a temperature of 41°. Glycidol, as thrice distilled in a vacuum in a stream of dry nitrogen, has d^{25} 1.1143 and n_D^{25} 1.4302. Thus purified it does not reduce Fehling's solution, nor does it give a mirror with ammoniacal silver nitrate either at room temperature or on warming. Tests for the isomeric acetol are negative. Glycidol is fairly stable, when pure, toward distilled water or absolute alcohol, even when heated on a steam-bath for an hour. It is slowly polymerized by pyridine, with evolution of heat, to a water-soluble black tar. With solid calcium chloride it polymerizes more rapidly, with great evolution of heat, to a water-soluble red tar. Several of the properties described by the writers are at variance with the previous literature. Thus Hanriot[8] reports that glycidol is insoluble in benzene and is polymerized by a trace of moisture. Gegerfelt[2] and Breslauer[2] state that it gives a mirror with ammoniacal silver nitrate, and other such references are found. It is evident that the glycidol used by the majority of investigators has been of doubtful purity.

Phenylurethan of Glycidol.—Equimolecular amounts of phenyl isocyanate and glycidol are heated on a steam-bath in ethereal solution for twelve hours. On removal of the ether an oil is obtained which solidifies when stirred with cold water. It is soluble in ether, alcohol and acetone, and insoluble in water and cold petroleum ether. It crystallizes from high-boiling petroleum ether in colorless needles which melt at 60°. The yield is over 90%.

Anal. Calcd. for $C_{10}H_{11}O_3N$: N, 7.25. Found: N, 7.20, 7.20.

α-Naphthylurethan of Glycidol.—Equimolecular amounts of a-naphthyl isocyanate and glycidol are heated on the steam-bath for twelve hours in the absence of a solvent. By dissolving the residue in acetone and then adding cold water, the solid urethan is obtained in good yields. It may be purified by recrystallization from high-boiling petroleum ether, out of which it separates in colorless needles which melt at 102°. The solubilities are similar to those of the phenylurethan.

Anal. Calcd. for $C_{14}H_{15}O_3N$: N, 5.76. Found: N, 5.57, 5.76.

Summary

1. The writers have prepared the phenylurethans of the isomeric glycerol a- and β-monochlorohydrins, and have found that these derivatives are suitable for a qualitative differentiation of the two forms.

2. Glycerol a-monochlorohydrin has been prepared by a new and simple procedure which gives yields considerably higher than those heretofore obtained.

3. Various methods for the preparation of glycidol, or epihydrin alcohol, have been investigated and a method is described whereby pure glycidol may be obtained in yields of 90% through the interaction of monochlorohydrin and metallic sodium.

4. The properties of glycidol have been described, and attention called to several errors found in the previous literature.

5. The phenyl- and α-naphthylurethans of glycidol have been prepared and found suitable for its identification.

NEW HAVEN, CONNECTICUT

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[8] Hanriot, *Ann. chim.*, *[5]* **17**, 62 (1879).

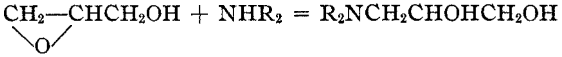
[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

STUDIES OF GLYCIDOL. II. REACTIONS WITH SECONDARY AMINES[1]

BY T. H. RIDER WITH A. J. HILL

RECEIVED JULY 24, 1929 PUBLISHED APRIL 7, 1930

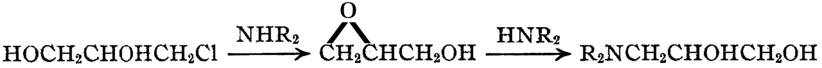
The writers have pointed out in a previous communication[2] that glycidol, I, should be particularly useful in synthetic work by reason of the activity of its ethylene oxide ring. This paper, the second in the series, deals specifically with the action of glycidol on secondary amines. Since the amino-alcohols which are thus formed are peculiarly suited as intermediates for the preparation of amino-esters related to those of the procaine type, the reaction has been carefully studied and the method of procedure applied to the synthesis of several dialkylaminopropanediols, II.



$$\underset{\diagdown O \diagup}{\mathrm{CH_2{-}CH}}\mathrm{CH_2OH + NHR_2 = R_2NCH_2CHOHCH_2OH}$$

I II

Roth[3] has prepared two of these compounds by the interaction of glycerol-a-monochlorohydrin and secondary amines. His procedure requires heating the reactants in a bomb tube at 100° for five to six hours. While the evidence is not conclusive, the mechanism[4] of this reaction is believed by many to be as follows



$$\mathrm{HOCH_2CHOHCH_2Cl} \xrightarrow{\mathrm{NHR_2}} \overset{\mathrm{O}}{\mathrm{CH_2CH}}\mathrm{CH_2OH} \xrightarrow{\mathrm{HNR_2}} \mathrm{R_2NCH_2CHOHCH_2OH}$$

While there are a few articles in the literature dealing with reactions of glycidol and similarly constituted compounds such as epichlorohydrin with basic amines, there is but one investigator who has prepared dialkylaminopropanediols by this method. Knorr[5] has treated dimethyl- and diethylamines with glycidol, obtaining in each case the same product that was given by the corresponding reactions with monochlorohydrin, thus substantiating in part the above-mentioned hypothesis. The reaction of Knorr is the more practicable since the free base rather than the hydrochloride is formed in the reaction and may be directly distilled or crystallized. Knorr's procedure requires mixing of the reactants and cooling of the reaction mixture during a period of twenty-four hours.

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[1] Constructed from part of the thesis presented by T. H. Rider to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

[2] Rider and Hill, THIS JOURNAL, 52, 1521 (1930).

[3] Roth, *Ber.*, 15, 1149 (1882).

[4] An interesting test of this theory lies in the reaction of glycerol-β-monochlorohydrin with secondary amines. If the products are identical, the theory is substantiated. An investigation of this reaction is being undertaken by one of us.

[5] Knorr, Ber., 32, 757 (1899).

While the method of Roth is the less satisfactory of the two, it may be greatly simplified. Instead of carrying out the reaction in a bomb tube, the writers have found it to proceed quite satisfactorily upon merely warming the chlorohydrin and amine for a short time under a reflux condenser. This same procedure suffices in the reaction between glycidol and secondary amines. In this case, however, there is a very important side reaction—that of the polymerization of the glycidol. Both the polymerization of glycidol by the amine, and the addition of the amine to glycidol proceed rapidly under the same general conditions. When diethylamine is added slowly to glycidol, during heating on a steam-bath, no diethylaminopropanediol can be isolated. If, on the other hand, glycidol is slowly added to boiling diethylamine, 90% yields of diethylaminopropanediol may be obtained. The presence of a sufficient excess of the amine in the reaction mixture may be insured, in most cases, by the slow addition of glycidol, in such fashion that there is at no time an appreciable amount of unreacted glycidol in the reaction mixture. We have found that the tendency to polymerize glycidol is much greater in the cases of diethyl- and dimethylamines, than with amines of higher molecular weight. In these latter cases, therefore, we have used a mole and a half of amine to one of glycidol. The yields are materially decreased if this excess of amine is not used. The greater tendency of amines of lower molecular weight to polymerize glycidol is also shown in the progressive increase in yields by the use of the higher amines.

Dimethylaminopropanediol forms a picrate and a quaternary ammonium salt with methyl iodide, both precipitating soon after alcoholic solutions of the reactants are mixed. These reactions have both been described by Knorr; our quaternary salt melting at 134–136° corresponds to that obtained by him. Our picrate, on the other hand, prepared by the same method melts at 126–128°, while Knorr gives a melting point of 160° for this substance. Although this investigator describes a picrate of the diethylaminopropanediol, the writers have been unable to prepare this compound. Furthermore, we have found it impossible to prepare either the picrate or the quaternary salts of the other higher aminodiols. This is possibly to be attributed to a rapid loss of basicity, or to steric influences attendant upon increase in size of the groups on nitrogen.

The action of acid chlorides and isocyanates on the dialkylaminopropanediols will be discussed in a subsequent paper.

Experimental Part

General Procedure for the Preparation of the **1-Dialkylamino-2,3-propanediols.**—The secondary amine is heated to a temperature somewhat below its boiling point—or with the higher amines on a steam-bath—in a three-necked round-bottomed flask equipped with mercury-sealed mechanical stirrer, a reflux condenser and a dropping funnel. During stirring, glycidol is slowly added from the dropping funnel, the rate of addition being so regulated that the amine does not reach its boiling point. In the case of dimethyl- and also diethylamine, one and one-half moles of amine are used to one mole of glycidol. In all other cases the reactants are used in 1:1 molar ratio. The glycidol should not be added through the condenser, since the traces of amine there encountered cause a relatively large amount of polymerization. The liquid products are distilled in vacuo. Piperidinopropanediol solidifies when the reaction mixture cools, and it is then recrystallized from acetone. The experimental data relating to the aminodiols are given in Table I.

TABLE I

DIALKYLAMINOPROPANEDIOLS

-Aminopropanediols	Formula	Nitrogen, % Calcd.	Found		Yield, %	B. p., °C.	Pressure mm.
Dimethyl-	$C_5H_{13}O_2N$	11.76	11.78	11.75	82	111	15"
Diethyl-	$C_7H_{17}O_2N$	9.52	9.58	9 61	90	106	3
Di-n-propyl-	$C_9H_{21}O_2N$	8.00	8.13	7.86	92	143	9
Di-isobutyl-	$C_{11}H_{25}O_2N$	6.90	6.96	6.96	94	122	2
Di-n-amyl-	$C_{13}H_{29}O_2N$	6.06	6.10	5.99	95	149	2
Piperidino-	$C_8H_{17}O_2N$	8.80	8.65	8.72	96.5	...	..[b]

[a] A 30% aqueous solution of dimethylamine was used in this reaction. [b] Piperidinopropanediol melts at 83°.

Picrate of Dimethylaminopropanediol.—The diol and picric acid are mixed in absolute alcohol solution and allowed to stand. The picrate precipitates from the solution and after filtration is purified by crystallization from absolute alcohol; m. p. 126–128°.

Anal. Calcd. for $C_{11}H_{16}O_9N_4$: N, 16.1. Found: N, 16.0, 16.0.

Summary

1. The reaction between glycidol and secondary amines has been studied.

2. A series of dialkylaminopropanediols has been prepared in yields which average over 90% of the theoretical.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

THE EFFECT OF ORGANIC BASES UPON THE EXTENT AND MECHANISM OF THE REDUCING ACTION OF SODIUM METHYLATE ON NITROBENZENE AND AZOXYBENZENE[1]

BY H. SHIPLEY FRY AND PAUL E. BOWMAN

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Introduction

In a recent study of the reducing action of sodium methylate upon nitrobenzene in methyl alcohol solution, Fry and Cameron[2] have shown quantitatively that the extent to which Klinger's[3] reaction

$$4C_6H_5NO_2 + 3CH_3ONa \longrightarrow 2(C_6H_5N)_2O + 3HCOONa + 3H_2O \qquad (A)$$

proceeds, as measured by the formate yield, was progressively decreased by the addition of increasing quantities of water, but when increasing quantities of pyridine, an organic base, were added, the extent of the reduction was progressively increased. Furthermore, it was found that in the presence of pyridine, azoxybenzene was partially reduced to azobenzene, according to the equation

$$2C_6H_5NO_2 + 2CH_3ONa \longrightarrow C_6H_5N{=}NC_6H_5 + 2HCOONa + 2H_2O \qquad (A')$$

In order to interpret these results, the following equations were proposed to represent the mechanism of the reducing action of sodium methylate.

$$\begin{array}{llll}
 & 3CH_3ONa + 3HOH & \longrightarrow 3CH_3OH + 3HONa & (x) \\
 & 3CH_3OH + 3NaOH & \longrightarrow 3HCOONa + 12H & (y) \\
 & 4C_6H_5NO_2 + 12H & \longrightarrow 2(C_6H_5N)_2O + 6H_2O & (z) \\
\Sigma(x), (y), (z) & 4C_6H_5NO_2 + 3CH_3ONa & \longrightarrow 2(C_6H_5N)_2O + 3HCOONa + 3H_2O & (A)
\end{array}$$

The summation of Equations x, y and z is Klinger's equation **(A).** It should be noted in passing that the intermediate equation (y) involving the acidic dissociation of sodium hydroxide is an example of a general type equation, $R(H)_n + n\text{HONa} \longrightarrow R(\text{ONa})_n + nH_2$, evidence for which has been given in previous papers.[4]

Consequently, any factor that hinders the acidic dissociation of sodium hydroxide, such as the addition of water, which promotes basic dissociation, limits the extent to which the intermediate equation (y) progresses, and hence limits the yield of formate. This was found to be true. On the other hand, the addition of basic pyridine would favor acidic dissociation and increase the extent of the reaction, as was also observed.

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[1] A synopsis of a thesis presented to the Faculty of the Graduate School, University of Cincinnati, by Paul E. Bowman, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Fry and Cameron, THIS JOURNAL, 49,864 (1927).

[3] Klinger, *Ber.*, 15, 866 (1882).

[4] Fry, Schulze and Weitkamp, THIS JOURNAL, 46,2268 (1924); Fry and Schulze, *ibid.*, 48, 958 (1925); Fry and Otto, *ibid.*, 50, 1120 (1928); Fry and Schulze, *ibid.*, 50, 1131 (1928); Fry and Otto, *ibid.*, 50, 1138 (1928).

To test further the validity of this proposed explanation of the reducing action of sodium methylate, based upon the apparent acidic dissociation of sodium hydroxide, experiments with five other bases were conducted.

Experimental

The previously described standardized methods of procedure and analysis,[2] in effecting the reduction of nitrobenzene and azoxybenzene with sodium methylate, in methyl alcohol solution, were again employed. In the first place, three independently repeated reductions of nitrobenzene, each in duplicate and with no organic base present, gave checks varying by not more than 1% and averaging 88.45% of the theoretical yield of sodium formate according to Klinger's equation (A). This figure is used as a standard for comparison in all subsequent experiments in measuring the extent of the reduction, calculated from yields of sodium formate.

Reductions of (a) nitrobenzene and (b) azoxybenzene were conducted in *a* reaction mixture of 250-cc. volume prepared in duplicate and containing sodium methylate, made by dissolving **17.3** g. of sodium in methyl alcohol, together with either 0.2 mole of nitrobenzene or 0.1 mole of azoxybenzene incorporated with $^1/_8$, $^1/_4$, $^1/_2$ or $^3/_4$ mole of each one of the five organic bases used, namely, (A) aniline, (B) monomethylaniline, (C) dimethylaniline, (D) quinoline and (E) iso-amylamine. This entailed a total of eighty separately conducted reductions.

The reaction mixtures were heated in 500-cc. round-bottomed flasks, with reflux condensers, on an actively boiling water-bath for five hours. The reaction mixtures were then treated as described in a previous paper.[2] The extents of the reduction of both nitrobenzene and azoxybenzene were

TABLE I

SUMMARY OF DATA: EFFECTS OF ORGANIC BASES UPON THE EXTENT OF REDUCTION OF NITROBENZENE

Moles of organic base	A	B	C	D	E
	Extent of reduction, %				
	Aniline	Monomethyl-aniline	Dimethyl-aniline	Quinoline	Iso-amylamine
$^1/_8$	96.85	91.70	93.93	95.62	63.45
$^1/_4$	99.26	98.61	98.95	102.66	40.70
$^1/_2$	98.28	103.06	105.56	107.62	38.22
$^3/_4$	94.26	104.44	107.12	113.02	51.75

TABLE II

SUMMARY OF DATA: EFFECTS OF ORGANIC BASES UPON THE EXTENT OF REDUCTION OF AZOXYBENZENE

Moles of organic base	A	B	C	D	E
	Extent of reduction, %				
	Aniline	Monomethyl-aniline	Dimethyl-aniline	Quinoline	Iso-amylamine
$^1/_8$	3.00	3.52	3.43	3.53	3.00
$^1/_4$	3.38	4.00	3.47	4.80	2.61
$^1/_2$	4.18	4.77	7.30	6.33	2.76
$^3/_4$	4.93	5.46	8.72	7.43	2.52

calculated in terms of the yield of sodium formate, using Equation **A** above for the nitrobenzene reduction and Equation **A'** above for the azoxybenzene reduction.

Since the checks obtained in every reduction conducted in duplicate differed less than 1%, the yields of sodium formate are averaged for the duplicate reductions. These averages are recorded in Tables I and II.

Discussion of Data

In every reduction of nitrobenzene, Table I, the presence of an organic base, with the exception of iso-amylamine, increased markedly the extent of the reduction beyond the normal 88.45% when no organic base was present. With the exception of iso-amylamine and aniline, the increase in the extent of the reduction follows the order of the increasing molar concentrations of the bases present and their respectively increasing basic properties.

The decrease in the yields of sodium formate when aniline was present (Column **A**, Table I) is probably due to the fact, observed by Baeyer,[5] that nitrosobenzene, an intermediately formed reduction product of nitrobenzene, reacts with aniline according to the equation $C_6H_5NO + C_6H_5NH_2 \longrightarrow C_6H_5N{=}NC_6H_5 + H_2O$, and produces no sodium formate.

The peculiar behavior with iso-amylamine will be considered in detail later.

The data of Table II show that azoxybenzene is somewhat susceptible to reduction to azobenzene by sodium methylate, which is oxidized to sodium formate provided an organic base is present. This serves to explain the partly increased yields of sodium formate and is in harmony with the assumption that organic bases favor acidic dissociation of sodium hydroxide, thereby effecting reduction of azoxybenzene to azobenzene—a *reduction which does not occur in the absence of an organic base.*

Here also, with the exception of iso-amylamine, the increase in the extent of the reduction follows the order of increasing molar concentrations of bases present, but quinoline, which is more basic than dimethylaniline, effected less reduction than the latter when $^1/_2$ and $^3/_4$ moles were present. These anomalies are reserved for future investigation..

The Exceptional Effect of Iso-amylamine

Iso-amylamine being more basic than the other four bases used should have greatly increased the yield of sodium formate, but the low yields of formate (Column E, Table I) were entirely out of harmony with the expected results and, furthermore, the amount of azoxybenzene was greatly in excess of that corresponding to the sodium formate obtained.

The key to these anomalies was the finding of *formaldehyde* in the reaction mixture *in combination with iso-amylamine.* When the azoxybenzene–

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[5] **Baeyer,** *Ber.*, **7, 1639** (1874).

benzene extract of the reaction mixture was treated with dilute sulfuric acid, the presence of formaldehyde was shown by its odor and characteristic reactions. When the acid extract was neutralized, the presence of iso-amylamine was attested by its odor. This is in line with the work of Henry,[6] who has shown that when a primary amine reacts with formaldehyde, a compound is formed (in this case, iso-amylmethylene-imide) which, upon addition of dilute acids, is resolved into the amine and formaldehyde.

The finding of formaldehyde in the reaction mixture is confirmation of the intermediate type reaction equation previously postulated[4] and according to which the equation for the reaction can be developed as follows:

$$
\begin{aligned}
&3CH_3OH + 3NaOH \longrightarrow 3CH_3ONa + 3H_2O && (x)\\
&3CH_3ONa + 3HONa \longrightarrow 3CH_2(ONa)_2 + 6H && (y)\\
&3CH_2(ONa)_2 + 3H_2O \longrightarrow 3CH_2O + 6NaOH && (z)\\
&2C_6H_5NO_2 + 6H \longrightarrow (C_6H_5N)_2O + 3H_2O && (z')\\
\Sigma(x), (y), (z), (z')\ &2C_6H_5NO_2 + 3CH_3OH \dashrightarrow 3CH_2O + (C_6H_5N)_2O + 3H_2O && (B)
\end{aligned}
$$

This equation (B) accounts for the presence of formaldehyde in the reaction mixture and also, since no sodium formate is formed as in the Klinger equation (A), for the yield of azoxybenzene in excess of that indicated by the yield of sodium formate. The determination of the amount of formaldehyde combined with iso-amylamine in the reaction mixture would serve to measure the extent of the concurrence of Reaction B.

Quantitative Determination of Formaldehyde Combined with Iso-amylamine.—The following method was devised for estimating quantitatively the amounts of formaldehyde combined with the iso-amylamine in the reaction mixtures, depending upon the fact that iso-amylamine, analogously to ammonia, reacts with mercuric chloride to give a white precipitate of mercuric iso-amylamidochloride. The azoxybenzene–benzene extracts of the reaction mixtures were treated with dilute sulfuric acid, the separated acid solution was diluted to 500 cc., and 10-cc. aliquot portions of this solution, containing iso-amylamine sulfate and free formaldehyde, were saturated with mercuric chloride. Then, as dilute sodium hydroxide solution was added, drop by drop, the iso-amylamine was set free and combined with mercuric chloride, precipitating mercuric iso-amylamidochloride. Further addition of sodium hydroxide was continued until all the excess mercuric chloride was converted to mercuric oxide, but care must be taken to avoid an excess of sodium hydroxide since mercuric oxide is reduced by formaldehyde in a too alkaline solution. After filtration, the filtrate was neutralized and its formaldehyde content determined by the standard hydrogen peroxide method.[7]

Solutions of known content of the iso-amylamine–formaldehyde compound gave check results by this new method.

Determination of the Distribution of the Reduction of Nitrobenzene between Two Concurrent Reactions.—Since nitrobenzene in the presence of iso-amylamine is reduced according to the following equations

$$
\begin{aligned}
&4C_6H_5NO_2 + 3CH_3ONa \longrightarrow 2(C_6H_5N)_2O + 3HCOONa + 3H_2O && (A)\\
&2C_6H_5NO_2 + 3CH_3ONa \longrightarrow (C_6H_5N)_2O + 3CH_2O + 3NaOH && (B)
\end{aligned}
$$

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[6] Henry, *Ber.* (Ref.), 26,934 (1893).

[7] "J. Assoc. Official Agr. Chemists," 1916, p. 75.

and since the quantities of sodium formate and formaldehyde, respectively, produced have been determined, it is possible to calculate therefrom the extent to which nitrobenzene is reduced in conformity with each of these respective reactions.

In Table III the determined and the calculated yields in their relationships to the concurrent reactions (A) and (B) are fully tabulated.

TABLE III

DATA ON REDUCTION OF NITROBENZENE ACCORDING TO CONCURRENT EQUATIONS (A) AND (B)

A Isoamyl-amine, moles	B Distribution Equations, A and B	C HCOONa Eq. A found, g.	D HCHO Eq. B found, g.	E $(C_6H_5N)_2O$ calcd., g.	F $C_6H_5NO_2$ calcd., g.	G $C_6H_5NO_2$ reduced, %	H Total reduction, Eq. A and Eq. B, %
$^1/_8$	A	6.4747	....	12.5685	15.6213	63.50	88.74
	B	....	2.2714	4.9917	6.2085	25.24	
$^1/_4$	A	4.1517	....	8.0591	10.0129	40.70	87.22
	B	....	4.1868	9.2109	11.4438	46.52	
$^1/_2$	A	3.8992	....	7.5680	9.4039	38.22	93.43
	B	....	4.9690	10.9318	13.5812	55.21	
$^3/_4$	A	5.2786	....	10.2467	12.7310	51.75	86.61
	B	....	3.1379	6.9033	8.5678	34.86	

The data in Column H show that the nitrobenzene is more extensively reduced in the presence of iso-amylamine than is indicated by the corresponding data in Table I, Column E, which, it should be recalled, relate only to the yield calculated as formate on the basis of the occurrence of Reaction A. In Column F, Table III, a marked anomaly is noted when $^3/_4$ mole of iso-amylamine was present in that Reaction A is more extensive than Reaction B. This unexpected result has not yet been explained and is reserved for further investigation as a special study.

To check and establish further the concurrence of Reactions A and B, the actual amounts of azoxybenzene found in reaction mixtures with $^1/_8$ and $^1/_2$ mole of iso-amylamine present, were recovered, purified and weighed. The *actual yields* of azoxybenzene were found to be practically equal to the sum of the *calculated yields* of azoxybenzene formed in conformity with the concurrent reactions (A) and (B). Table IV embodies the data.

TABLE IV

DATA CONFIRMING CONCURRENT REACTIONS (A) AND (B)

Iso-amyl-amine, moles	HCOONa (Eq. A) found, g.	HCHO (Eq. B) found, g.	$(C_6H_5N)_2O \simeq$ HCOONa (Eq. A) calcd., g.	$(C_6H_5N)_2O \simeq$ HCHO (Eq. B) calcd., g.	$(C_6H_5N)_2O \simeq$ (Eq. A) + (Eq. B) calcd., g.	$(C_6H_5N)_2O$ found, g.	$\frac{\text{Calcd., g.}}{\text{Found, g.}}$ %
$^1/_8$	6.4747	2.2714	12.5685	4.9971	17.5656	17.53	100.20
$^1/_2$	3.8992	4.9690	7.5680	10.9318	18.4998	18.79	98.45

General Conclusions

1. The presence of an organic base markedly increases the extent of the reduction of nitrobenzene to azoxybenzene by sodium methylate.

2. The presence of an organic base causes some further reduction of azoxybenzene to azobenzene.

3. Increasing molar concentrations of organic bases present in the reaction mixtures caused increased percentage reductions of nitrobenzene and of azoxybenzene.

4. Formaldehyde, one of the predicted intermediate products of the reaction mechanism scheme, is formed in the reaction mixtures containing iso-amylamine, with which it combines to form iso-amylmethylene-imide.

5. The formaldehyde so combined with the iso-amylamine can be isolated and quantitatively determined according to a newly proposed method.

6. The yield of formaldehyde conforms to the equation for a new reaction, $2C_6H_5NO_2 + 3CH_3ONa \longrightarrow (C_6H_5N)_2O + 3CH_2O + 3NaOH$, which is concurrent with Klinger's reaction, $4C_6H_5NO_2 + 3CH_3ONa \longrightarrow 2(C_6H_5N)_2O + 3HCOONa + 3H_2O$.

7. The distribution of the extent of the reduction of nitrobenzene in the presence of iso-amylamine has been calculated and found to conform to the equation for the concurrent reactions noted in (6).

8. The observations of this study afford additional evidence for the previously proposed reaction mechanism schemes involving the apparent acidic dissociation of sodium hydroxide.

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[CONTRIBUTION PROY THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE ACTION OF DIAZOMETHANE ON THE PYRIMIDINE CONSTITUENTS OF NUCLEIC ACIDS

BY FRANCIS H. CASE WITH ARTHUR J. HILL

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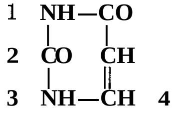
Notwithstanding the large amount of work which has been devoted to the study of nucleic acids, the position of attachment of the carbohydrate nucleus to the pyrimidine constituents (uracil, I, cytosine, II and thymine, III) still awaits definite solution, although the burden of evidence[1] appears to be increasingly in favor of linkage in position **3** rather than 4.



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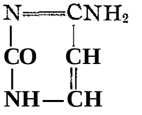

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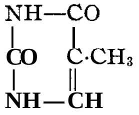

III

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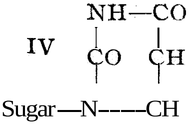
[1] Burian, *Ber.*, 37, 708 (1904); Johnson and Clapp, *J. Biol. Chem.*, 5, 163 (1908); Wheeler and Johnson, *ibid.*, 3, 183 (1907); cf. Ref. 2.

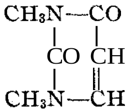
Color tests, as well as reactions, have pointed to this conclusion. For example, the recent work of Levene[2] and his co-workers on the behavior of uracil and its nucleoside uridine, IV, toward either hydrazine or phenylhydrazine (after pretreatment with bromine) is extremely significant in their bearing on this point.

IV



The chief desideratum in solving this interesting problem is a reagent, or reaction, which will effectively introduce a substituent into position 3 (or 4), provided, of course, the position is not already occupied by the sugar residue. An attempt to this end was made by Levene[3] in his alkylation experiments on the silver, lead and alkali salts of the nucleosides, cytidine and uridine. Unfortunately the results were inconclusive.

Diazomethane is not infrequently a useful reagent for methylation, as it may be used in anhydrous neutral media and at room temperatures. It would seem that by appropriate choice of conditions, it might be possible to use this reagent for the methylation either of nucleic acids or their partial breakdown products, the nucleotides, or nucleosides. Subsequent examination of the methylated pyrimidines, after hydrolysis of the methylated complex, should throw some light on the position of the sugar linkage. Thus if 1,3-dimethyl-uracil, V, were obtained, one would be justified in assuming linkage in position 4. On the other hand, the isolation of 1-methyluracil would be evidence of a sugar linkage at position 3.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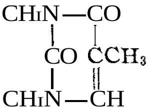
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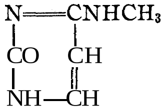
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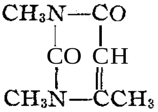
VIII

Although it is our ultimate purpose to investigate the methylation of the nucleic acids, or the nucleosides, it has been necessary first to examine the behavior of the pyrimidine constituents alone toward diazomethane. This paper, then, deals largely with this phase of the problem although some preliminary data on the methylation of yeast nucleic acid are also given.

Uracil, thymine and cytosine have been treated with diazomethane under various conditions, which are described below. In the cases of uracil and thymine, the methylation proceeded smoothly and there was no evidence of the formation of methylated products, other than 1,3-dimethyluracil, V, and 1,3-dimethylthymine, VI, respectively. The action of diazomethane on 4-methyluracil was also investigated in order to determine whether or not substitution in position 4 would retard methylation in position 3. However, this compound methylated quite as readily as uracil

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[2] Levene, *J. Biol. Chem.*, *63*, 653 (1925); Levene and Bass, *ibid.*, 71, 167 (1926); Levene, Bass and Simms, *ibid.*, 70,229 (1926).

[3] Levene and La Forge, *Ber.*, 45,608 (1912).

itself, giving 1,3,4-trimethyluracil, VIII. With cytosine, methylation was very hard to achieve; in fact the slowness and incompleteness of the reaction, and the difficulty in removing polymerized diazomethane from the ether-soluble material, made the investigation of the methylation products very troublesome. However, after considerable experimentation a rather small amount of monomethylcytosine, VII,[4] was isolated. A very interesting observation was made in regard to the ether-insoluble, non-methylated residue. On crystallization from aqueous acetone, this material separated in the form of short prismatic aggregates, quite different from the usual platy, or occasionally spear-shaped, crystals of cytosine. This prismatic variety possessed, however, the same melting point and degree of hydration as ordinary cytosine, and yielded the same picrate. After *dehydration* and crystallization from water or aqueous acetone, conversion to the ordinary cytosine took place. The prismatic variety could not, on the other hand, be prepared by crystallization of ordinary cytosine. So far as the writers are aware, this action of diazomethane is quite unique. The existence of two crystalline forms of cytosine is interesting in view of the fact that phenyl isocytosine has been shown to occur in four different forms.[5]

Preliminary experiments on the methylation of yeast nucleic acid did not lead to any definite evidence concerning the position of attachment of sugar to the pyrimidines. Although the nucleic acid apparently combined with a relatively large amount of diazomethane, subsequent hydrolysis of the methylated material yielded neither methylated nor unmethylated pyrimidines, when the usual procedure for isolation was used. Seemingly the long contact with a large excess of diazomethane had produced profound side reactions[6] A change in the conditions of methylation will be studied.

Experimental Part

Diazomethane.—The diazomethane used in this investigation was prepared from nitrosomethylurethan by von Pechmann's method.[7] The concentration of the ethereal solutions of diazomethane was determined by Marshall and Acree's method,[8] which involves treatment of the unknown solution with an excess of *m*-nitrobenzoic acid, followed by titration of the unmethylated acid with standard alkali.

Methylation of Uracil. **1,3-Dimethyluracil,** V.—In all experiments on the methylation of uracil, 1-g. samples of this substance were treated with ethereal diazomethane solutions of appropriate strengths in 250-cc. flasks provided with air condensers. The progress of reaction in the different flasks was followed from day to day, with particular regard to the disappearance of the yellow color of the reagent and to the solution of the uracil. Some typical data are given in Table I.

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[4] *Cf.* Case and Hill, THIS JOURNAL, 51, 1590 (1929).

[5] Johnson and Hill, *ibid.*, 36, 1201 (1914).

[6] Cf. Levene, *J. Biol.* Chem., *55*, 437 (1923).

[7] Von Pechmann, ***Ber.***, 28, 855 (1895).

[8] Marshall and Acree, *ibid.*, 43, 2323 (1910).

TABLE I

THE ACTION OF DIAZOMETHANE ON URACIL

Diazomethane[a] (mol. proportions)	1	3	4	6	1[d]
Time, days	6	5	6[c]	6[c]	1
Sther-sol. material,[b] g.	0.25	0 80	1.22	1.11	0.30

[a] In ether solution. [b] Calculated for complete dimethylation, 1.25 g. [c] Complete solution was effected and the color of the diazomethane had nearly disappeared. [d] With an equal volume of alcohol. Complete decolorization with only slight solution of uracil.

On completion of the designated period of methylation, the various ethereal solutions were filtered, and the filtrates evaporated to dryness. The last line in Table I gives the weight of the residues thus obtained. The figures are only close approximations of the amount of methylated material as the residues were contaminated to some extent with polymerized diazomethane.

The insoluble material, resulting from experiments in which methylation was not complete, melted in no case under 300°. The three possible nitrogen-methylated uracils have the following melting points, respectively: 1-methyluracil, 174–175°; 3-methyluracil, 223–226°; and 1,3-dimethyluracil, 121–122°. Uracil melts at 338°. There was apparently a complete absence of methylated products in the ether-insoluble portion.

The residues resulting from evaporation of the ethereal filtrates were carefully crystallized from a ligroin–absolute alcohol mixture. The products obtained from these crystallizations melted at 121°; mixtures of each with known samples of 1,3-dimethyluracil (m. p. 121°) melted at the same temperature, thereby establishing identity with the latter. In order to determine whether any momomethylated uracils were formed in the reaction, the mother liquors from the above described crystallizations were evaporated and the residues carefully crystallized from ligroin and absolute alcohol. Only 1,3-dimethyluracil could be obtained by this procedure. Irrespective, then, of the amount of the reagent used, diazomethane always reacts with uracil to form the 1,3-dimethyl derivative. The minimum amount necessary for complete methylation under these conditions is four moles.

Anal. (On the methylated product melting at 121°.) Calcd. for $C_6H_8O_2N_2$: N, 20.00. Found: N, 19.87.

Methylation of Thymine. 1,s-Dimethylthymine, **VI.**—In the experiments on the methylation of thymine, 2-g. samples of the substance were treated with 100 cc. of ethereal solutions of diazomethane (1 to 6 molecular proportions) in 250-cc. flasks equipped with air condensers. There was a steady decrease in the ether-insoluble residue attendant upon increase in the amount of diazomethane from one to six molecular proportions. In this latter case decolorization of the reagent was effected in ten days; the ether-soluble material weighed 2.56 g. and the ether-insoluble, 0.04 g. Complete methylation was accomplished under these conditions. It could also be brought about by the use of 2.25 molecular proportions of diazomethane in a closed system during continuous shaking. Under these conditions the time of methylation was materially reduced. An attempt to methylate in alcohol medium was unsuccessful as the reagent attacked the solvent too rapidly.

The melting points of the three nitrogen-methylated thymines are as follows: 1,3-dimethylthymine 153°, 1-methylthymine 202° and 3-methylthymine 280°. The tabulated results indicate in all experiments a complete absence of methylated products in the ether-insoluble residue, as this never melted below 300°, which is considerably above the melting point of either monomethylthymine. Only thymine was isolated from the ether-insoluble residue. Crystallization of the ether-soluble material from ligroin and alcohol gave in each experiment a product which was identical with 1,3-

dimethylthymine (m. p. 153°). An examination of the mother liquors from these crystallizations for monomethylated products revealed only further quantities of dimethylthymine.

Anal. (Kjeldahl). Calcd. for $C_7H_{10}O_2N_2$: N, 18.18. Found: N. 18.01, 18.02.

Methylation of 4-Methyluracil. 1,3,4-Trimethyluracil, VIII.—Two-gram samples of 4-methyluracil were treated with four molecular proportions of diazomethane in flasks provided with air condensers, After fifteen days, the 4-methyluracil had completely dissolved and there was a small residuum, which was apparently polymerized diazomethane. This was filtered off and the yellow solution evaporated to dryness. The residue thus obtained was crystallized from ligroin and absolute alcohol; it melted at 109° and was identical with 1,3,4-trimethyluracil (m. p. 109°). A typical experiment carried out under the above-described conditions gave the following results: ether-soluble material, 2.49; ether-insoluble material, 0.04 g.; m. p. of ether-soluble material, 109°.

Anal. Calcd. for $C_7H_{10}O_2N_2$: N, 18.18. Found: N, 18.01, 18.02.

The Action of Diazomethane on Cytosine.—In preliminary experiments, 2-g. samples of cytosine were placed in 250-cc. flasks and treated with quantities of diazomethane corresponding to 1, 2, 3, 4 and 5 molecular proportions. The methylation proceeded so slowly under these conditions that it became necessary to adopt a rather drastic procedure, namely, to carry out the reactions, during continuous shaking, in porcelain stoppered bottles, with large quantities of diazomethane, the reagent in certain experiments being replenished from time to time until there was no further decolorization. The data from typical experiments are given in Table II.

TABLE II

THE ACTION OF DIAZOMETHANE ON CYTOSINE

Diazomethane (mol. proportions)	7	10	13	15	15
Ether-insoluble material, g.	1.39	0.87	1.05	0.75	0.51
Ether-soluble material, g.	0.87	1.64	1.69	1.69	2.63
Time, days	17	25	4 months	4 months	33

A. A New Crystalline Form of Cytosine.—The insoluble material, after treatment with diazomethane, was filtered off and first examined for methylated cytosines by extraction with alcohol–petroleum ether. The amount of soluble material was negligible. The insoluble residue was then crystallized twice from aqueous acetone. The compound thus obtained was identical with cytosine in respect to its melting point, degree of hydration, analytical data and the melting point of its picrate. Under the microscope, however, it presented an entirely different appearance. The crystals of cytosine are normally quite platy, and occasionally of spear-shaped appearance, while the new form crystallized in peculiarly characteristic stout prisms. The two varieties melted unchanged when mixed; this was also true of their picrates. A number of attempts were made to produce this prismatic form by crystallization of ordinary cytosine under many conditions, but without success. On the other hand, when the new form was dehydrated, and then crystallized from water, or aqueous acetone, the ordinary or tabular form resulted. A comparison of the two forms is given in Table III.

TABLE III

COMPARISON OF THE TWO CRYSTALLINE FORMS OF CYTOSINE

Variety of cytosine	M. p., °C.	Hydrate, % N	Anhydrous, % N	Water, % H_2O	Picrate, m. p., °C.
Tabular (ordinary)	302–306	32.56	37.84	13.95	260–280
Prismatic (new)	306	32.60	37.70	13.69	260–280

B. 2-Oxy-6-methylaminopyrimidine, VII.—The writers had great difficulty in extracting a definite methylation product from the dark-colored residues resulting from evaporation of the ether solutions, after the insoluble residues had been filtered off. A very small amount of the picrate of 2-oxy-6-methylaminopyrimidine was isolated by the following procedure. Ether-soluble material from the methylation experiments was acidified with hydrochloric acid and the solution decolorized as much as possible with norite. After careful evaporation to dryness, the residue was taken up in 1% hydrochloric acid and the base precipitated by the addition of picric acid. The highly colored impure picrate was crystallized several times from aqueous methyl alcohol The small amount of crystals obtained in this manner melted at 220" and also at the same temperature when mixed with a sample of the picrate of synthetic 2-oxy-6-methylaminopyrimidine, (m. p. 220–225).[4] The former, like the latter, gave a positive test with the Wheeler–Johnson reaction,' and with the sulfanilic acid test,[1] thus showing the absence of a substituent in position 3.

We propose in subsequent work to accumulate sufficient ether-soluble methylated material to permit of thorough search for other methylated products.

The Action of Diazomethane on Yeast Nucleic Acid.—The yeast nucleic acid was prepared by Kowalevsky's[9] procedure. The sample isolated in this manner analyzed as follows

Nitrogen (Kjeldahl)	11.39	11.48
Phosphorus	5.97	6.25

Two ten-g. samples of the nucleic acid were placed in pressure bottles and each was treated during the course of three months with approximately 40 g. of diazomethane. The reagent was added in portions of about 4 g. whenever decolorization had occurred. The first addition of diazomethane was accompanied by vigorous evolution of nitrogen, probably by reason of its reaction with the phosphoric acid residues, but after this initial period of activity there was only gradual fading of the color. After methylation was considered to be complete, as evidenced by the persistence of the yellow color, the mixture was filtered and the filtrate evaporated to dryness. The weights of the ether-soluble portions in Samples 1 and 2 were, respectively, 5.90 and 6.80 g. and of the ether-insoluble portions, 6.0 and 7.40 g. Analysis of the ether insoluble material yielded the following results.

	Sample 1		Sample 2	
Nitrogen	8.45	8.60	9.84	9 83
Phosphorus	5.56	5.68	5.62	5.84

These data would indicate that there had been extensive combination with diazomethane. The nitrogen content decreased far more than that of phosphorus.

The soluble and the ether-soluble portions resulting from the reactions were separately hydrolyzed, but owing to the conditions (or duration) of methylation, profound changes had occurred and it was found impossible to isolate either methylated or unmethylated pyrimidines by application of one of the usual procedures.[10] A similar behavior of diazomethane was observed by Levene[11] in the methylation of xanthosine, and is well characterized in his statement to the effect that "the hydrolytic and oxidizing actions of diazomethane, and their mechanisms, deserve special investigation." This preliminary investigation has, therefore, served to emphasize the importance of using a medium and conditions for methylation which will accomplish this reaction in a shorter time and thus obviate destructive side reactions.

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[9] Kowalevsky, *Z. physiol. Chem.*, *69*, 240 (1910).

[10] Johnson and Brown, *J. Biol. Chem.*, 54, 731 (1922).

[11] Levene, *ibid.*, 55, 437 (1923).

Summary

1. A study has been made of the action of diazomethane on the cyclic ureides, uracil, thymine, cytosine and 4-methyluracil.

2. Uracil, thymine and 4-methyluracil were readily converted into their 1,3-dimethyl derivatives by the action of diazomethane.

3. Cytosine methylated very slowly; the unmethylated portion was a new crystalline variety of this compound; the methylated portion contained among other products a small quantity of 2-oxy-6-methylaminopyrimidine, which was isolated in the form of its picrate.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION NUMBER 404 FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY]

ACETOLYSIS OF CELLULOSE AND THE ISOLATION OF TWO CRYSTALLINE FORMS OF GLUCOSE PENTA-ACETATE[1]

BY C. S. WEBBER, C. J. STAUD AND H. LEB. GRAY

RECEIVED SEPTEMBER 5, 1929 PUBLISHED APRIL 7, 1930

Introduction

Glucose penta-acetate as an end-product of the acetolysis of cellulose is frequently mentioned: Weltzien and Singer,[2] Harold Hibbert,[3] Irvine and Soutar,[4] Freudenberg,[5] H. Ost.[6] In 1912 Klein[7] stated he believed the water-soluble products of acetolysis to be aceto-sulfates of dextrose or cellobiose. In the same year Ost[8] and Ost and Katayama[9] published two papers concerning the production of glucose penta-acetate in the acetolysis of cellulose.

The first note stated that acetolysis was carried to maximum water solubility. Ether extraction of the aqueous solution and reacetylation of the gum obtained with cold acetic anhydride and sulfuric acid yielded needles of glucose penta-acetate from alcohol. The second was concerned with the acetolysis of cellulose, hydrocellulose and alkali cellulose and in all cases after reacetylation penta-acetylglucose was obtained.

Ost in a more complete account of his work suggested that dextrose acetates are not to be looked for in the precipitate but in the ether ex-

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[1] Presented before the Division of Cellulose Chemistry at the 78th Meeting of the American Chemical Society, Minneapolis, Minnesota, September 9 to 13, 1929.

[2] Weltzien and Singer, *Ann.*, 443, 71 (1925).

[3] Hibbert, *J. Ind. Eng. Chem.*, 13, 256 (1921).

[4] Irvine and Soutar, *J. Chem. Soc.*, 117, 1489 (1920).

[5] Freudenberg, *Ber.*, 54, 771 (1921).

[6] Ost, *Ann.*, 398, 313 (1913).

[7] Klein, *Z. angew. Chem.*, 25, 1409–1415 (1912).

[8] Ost, *Chem.-Ztg.*, 36, 1099–1100 (1912).

[9] Ost and Katayama, *Z. angew. Chem.*, 25, 1467 (1912).

tract of the mother liquor. The gum obtained, which he claims is uncrystallizable, upon reacetylation yields glucose penta-acetate. The necessity for reacetylation Ost states is due to the partial saponification of the penta-acetylglucose by the sulfuric acid to uncrystallizable lower acetates. He found that higher concentrations of sulfuric acid gave rise to sulfo-acetates, 10% sulfuric acid yielding principally glucose tetra-acetate.

Freudenberg improved the acetolysis procedure by using no acetic acid. He showed that cellobiose octa-acetate is very resistant to acetolysis.

No statement has been found in the literature concerning the partition of the glucose penta-acetate between the precipitate and the mother liquor.

Mention is made[6] that glucose penta-acetate is very difficultly soluble in water but fairly soluble in the acidic mother liquor.

The authors have found that glucose penta-acetate may be isolated from the mother liquors from the recrystallization of cellobiose octa-acetate and from the chloroform extract of the aqueous mother liquor. Also glucose penta-acetate in the form of plates can be obtained in both cases, though in isolating the compound from the mother liquors of the cellobiose octa-acetate recrystallization, the plates changed to needles during their isolation. So far as is known, glucose penta-acetate has not been previously reported as crystallizing in any other form than as needles. A crystallographic study of these two forms of glucose penta-acetate is contemplated.

It appears significant that the formation of crystals of glucose penta-acetate in the gum took place only when, instead of water, the acetolysis mixture was poured into dilute sodium carbonate or hydroxide solution sufficient to neutralize the sulfuric acid present. This appears to confirm Klein's[7] statement concerning sulfo-acetates and Ost's[6] relative to the saponification of glucose penta-acetate by the sulfuric acid.

Experimental

Part I. The Isolation of Glucose Penta-acetate from the Acetolysis Precipitation Liquid without **Reacetylation.**—Five acetolyses were carried out. In each case 11 cc. of concentrated sulfuric acid (sp. gr. 1.84) was added to 80 cc. of acetic anhydride (Eastman Kodak Company, white label). The temperature was 5° during mixing. Twenty grams of cotton linters was added and the mass stirred continuously until a sirup was formed, which required approximately two hours. During this stage the temperature was kept below 60°. The sirup was then held at 41° (±0.5°) for twenty-two hours. The material from each preparation, a dark red thin liquid, was poured into water containing in each case **155** cc. of *2.5* N sodium hydroxide. In three preparations **1500** cc. was the total volume of the precipitation liquid and in two 3500 cc. each was used. The precipitates of crude cellobiose octa-acetate were filtered off and the weight before and after crystallization, as well as the melting points of the once crystallized products, were obtained. The data are given in Table I.

In later work it was found that the cellobiose octa-acetate precipitated in dilute alkali gave a higher melting point, after crystallizing once from ethyl alcohol, than did materials precipitated in water.

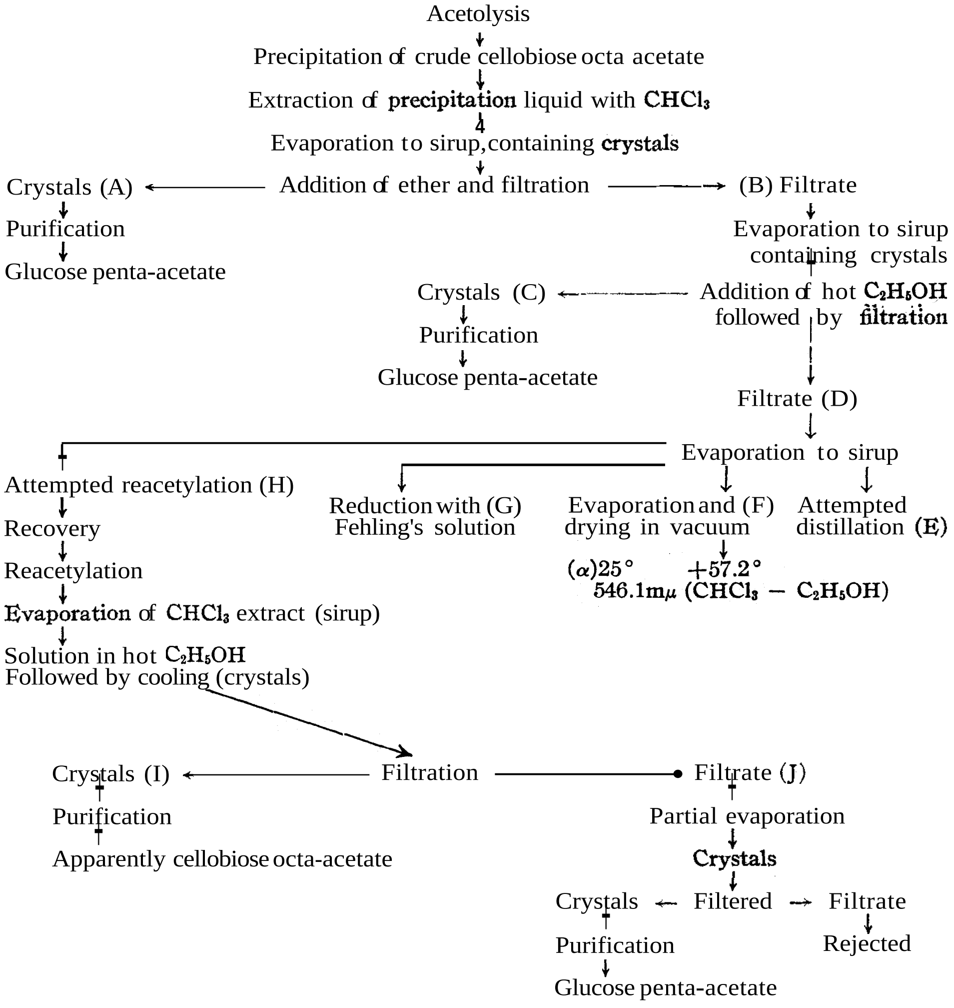
TABLE I

EXPERIMENTAL DATA

Preparation number	I	II	III	IV	V
Precipitate (crude), g.	20.2	20.3	17.2	17.0	16.0
Ppt. after cryst. from EtOH, g.	5.0	5.0	4.8	4.7	3.5
M. p. of crystals, uncorr., °C.	218–219	218–219	218–219	..	..

The liquors from which the crude cellobiose octa-acetate was removed were combined and extracted three times with chloroform, with the addition of a minute quantity of acetone to decrease the tendency to form emulsions. The chloroform solution was evaporated and a sirup containing crystals was obtained on standing. A small amount of ether was added and the crystals filtered off. These are designated as "A" in the diagram (see Fig. 1). They were recrystallized from hot ethyl alcohol; yield, 4 g. of

Figure I



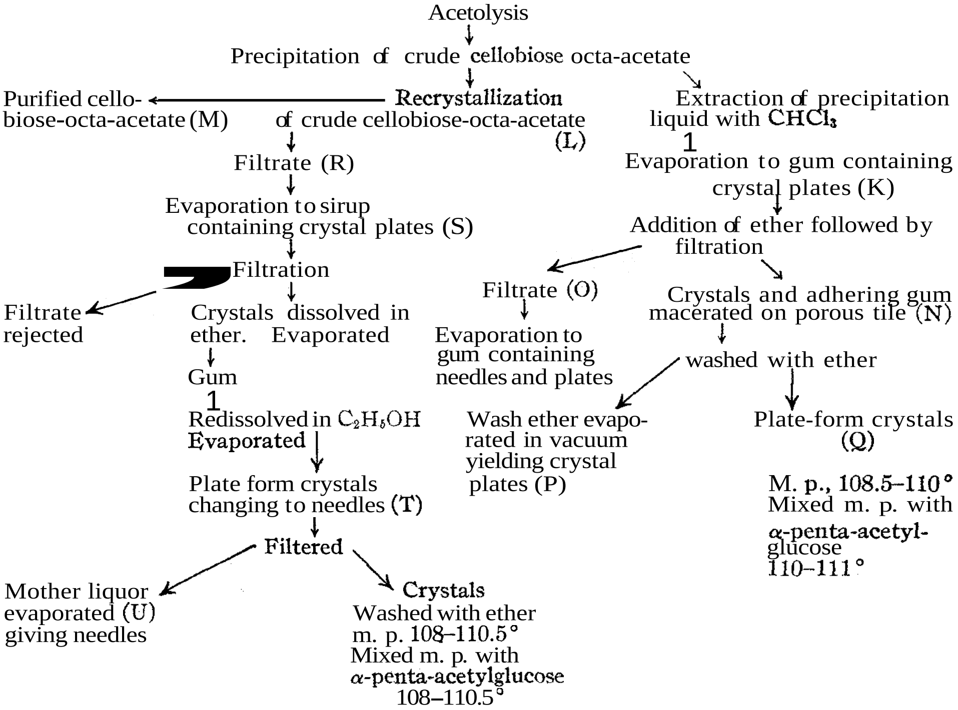
fine needles, m. p. 111–112°, specific rotation $122.5° at 25°, $c = 1$, $l = 1$, 546.1mμ line. These crystals correspond in melting point and optical rotation to glucose penta-acetate.

The filtrate in the diagram was evaporated to a gum containing crystals. The gum was dissolved in a minimum of hot ethyl alcohol and upon cooling crystals separated. These were filtered, washed with cold ethyl alcohol and dried on a porous tile; yield, 8 g. of fine needles, m. p. 110–111°, "C" in Fig. I. The acetyl content was 58.0% and the molecular weight in acetic acid 367, both of which appear to be in substantial agreement with the theoretical values of 57.8% and 390 for glucose penta-acetate.

To the filtrate from "C," "D" in Fig. I, was added an equal volume of water. Upon evaporation an emulsion resulted. Chloroform extraction yielded a sirup. A portion distilled at 6 mm. pressure (E in diagram) decomposed; a second portion was dried in a vacuum desiccator (F), dissolved in chloroformalcohol (85:15) by volume) and a specific rotation of +57.2° obtained (25°, 546.1mμ $c = 1$, and $l = 1$). A third part (G) with Fehling's solution showed strong reducing properties.

The remainder (H) was reacetylated, using acetic anhydride and sodium acetate, but the product after precipitation in water, extraction with chloroform and evaporation was a sirup. This was reacetylated with acetic anhydride and sulfuric acid. Crystals were observed in the solution, water was added and the sulfuric acid neutralized with sodium bicarbonate. The solution was extracted with chloroform and evaporated. The resulting light brown gum was dissolved in hot ethyl alcohol, cooled and a crystalline precipitate obtained. The crystals (I) were filtered, washed with cold ethyl alcohol and dried, giving needles of m. p. 220–221°, and a specific rotation of +42.0°.

Figure 11



The melting point of cellobiose octa-acetate is 226–227° and its specific rotation under similar conditions is +46.0°. The filtrate (J) was partially evaporated and the crystals were isolated. They were fine needles, m. p. 110–111°, indicating glucose penta-acetate.

Part II. Isolation and Identification of Two Crystalline Forms of a-Glucose Penta-acetate.—In earlier work on acetolysis (unpublished results) plate-form crystals were 'observed in the gum, "K," Figure II. Similar crystals had also been observed by Sir J. C. Irvine (informal discussion). Crystallization, if any, requires long standing at room temperature. Attempts to isolate these had previously met with failure.

Twenty-nine acetolyses were carried out, conditions were varied and three different types of cellulose material were used: cotton linters, rag paper without sizing and esparto pulp. The acetolysis was carried out as described in Part I, the temperature being varied from 136" for two and one-half minutes to 25° for fourteen days.

The yield of cellobiose octa-acetate obtained was higher when the reaction temperature was low, and the product could be more easily purified. Esparto pulp gave yields of cellobiose octa-acetate comparable with that from other sources.

The acetolysis mixture was poured into 1500 cc. of water alone and containing alkali as described in Part I.

The mother liquors were extracted with chloroform, the extract evaporated and a gum obtained in all cases. Upon standing for several days one of the gums contained plate-form crystals as shown in the photomicrograph Plate I. The usual crystals of or-glucose penta-acetate are given in Plate II.

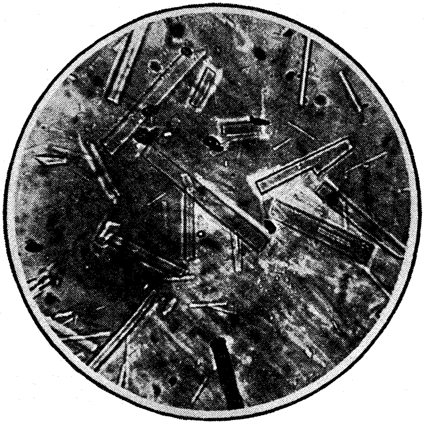


Plate 1.

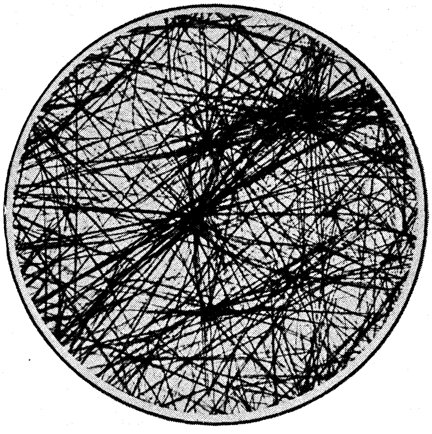


Plate 2.

The preparation which yielded plate-form crystals was made using unsized rag paper with acetolysis in an oil-bath at 113° until the internal temperature had risen to 109°. Precipitation was made in dilute alkali; yield, 35 g. (L); after crystallization from ethyl alcohol, five grams (M). The gum from extraction with chloroform and evaporation weighed 8.7 g. (K). To it a small amount of ether was added, with caution, since the crystals were fairly soluble in ether. The solution was filtered and the crystals with adhering gum (N) were worked on a porous tile with a spatula. The filtrate (O) was evaporated and a gum containing both plate and needle-form crystals obtained. The ether washings evaporated in vacuum yielded more crystal plates (P). The washed crystals (Q) melted at 108.5–110°; specific rotation in chloroform–alcohol (85:15 by volume) +112.5°, at 25° (546.1mμ line). This would indicate the plate-form crystals to be a-penta-acetylglucose.

Three melting points were made simultaneously. In one tube was placed a known sample of glucose penta-acetate, prepared as described in Part I; in the second tube, the plate-form crystals; and in the third, a mixture of the two. The melting points were **111.5, 110–111** and 108.5–110°, respectively.

The filtrate (R) was then examined. Evaporation at room temperature yielded plate-form crystals (S). These were removed by filtration, dissolved in ether and evaporated, giving a gum. This was taken up in alcohol and again evaporated at room temperature. Plate-form crystals (T) separated, changing in the course of two days mostly to the more usual needle-form of α-glucose penta-acetate. These were filtered off and washed with ether. Melting points of these crystals, of α-penta-acetylglucose and a mixture of these two were taken simultaneously. The melting points were **108–110.5, 111.5** and 108–110.5°, respectively. The filtrate (U) was observed to give a further yield of needle-like crystals upon evaporation.

Summary

1. Two crystalline forms of α-glucose penta-acetate have been isolated from the chloroform extract of the precipitation liquid of the acetolysis of cellulose, without reacetylation.

2. Further yields of glucose penta-acetate and of cellobiose octa-acetate have been obtained by the reacetylation of the gum obtained after isolation of crystalline glucose acetate, mentioned in 1.

3. α-Glucose penta-acetate has been isolated from the mother liquors of the crystallization of crude cellobiose octa-acetate obtained in the acetolysis of cellulose.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THERMAL DATA ON ORGANIC COMPOUNDS. VII. THE HEAT CAPACITIES, ENTROPIES AND FREE ENERGIES OF TWELVE AROMATIC HYDROCARBONS[1]

BY HUGH M. HUFFMAN,[2] GEORGE S. PARKS[3] AND ALBERT C. DANIELS[4]

RECEIVED SEPTEMBER 27, 1929 PUBLISHED APRIL 7, 1930

In the preceding paper[5] the results of a study of the heat capacities, entropies and free energies of some saturated, non-benzenoid hydrocarbons were reported. The present investigation is essentially similar but deals with aromatic hydrocarbons. We shall first present heat capacity data

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[1] This paper contains results obtained in an investigation of the heat capacities and free energies of some typical hydrocarbon compounds, listed as Project No. 29 of the American Petroleum Institute Research. Financial assistance in this work has been received from a Research fund of the American Petroleum Institute donated by The Universal Oil Products Company. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

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[4] American Petroleum Institute Research Assistant (part-time).

[5] Parks, Huffman and Thomas, THIS JOURNAL, 52, 1032 (1930).

for the following twelve compounds: benzene, ethylbenzene, *tert.*-butylbenzene, *o*-xylene, m-xylene, *p*-xylene, hexamethylbenzene, diphenyl, diphenylmethane, triphenylmethane, dibenzyl and naphthalene. We shall then utilize these data to calculate their molal entropies by the aid of the third law of thermodynamics. From the latter results, the corresponding free energy values will be derived.

Materials

Benzene.—The benzene was a very pure sample of "reagent quality" obtained from the Mallinckrodt Chemical Works. It was dried over phosphorus pentoxide and then carefully fractionated by distillation. The middle portion was next subjected to six successive fractional crystallizations. The final product gave a very sharp melting point (5.5') during the determination of the heat of fusion, indicating a high degree of purity.

Ethylbenzene and *Tert.*-**butylbenzene.**—These compounds were synthesized by the Friedel–Crafts reaction in the chemical laboratory of Johns Hopkins University. They were then purified by three fractional distillations. Mr. I,. M. Ellis, Jr., made the last two of these distillations, using a special still which had an eighteen-inch packed column with a heated jacket and reflux head. The ethylbenzene thus obtained boiled at 135.5–135.7° at 756 mm.; its specific gravity was 0.8639 at 23.4°/4°. For the *tert.*-butylbenzene the boiling temperature was 168.5 to 168.8° at 758 mm.; specific gravity, 0.8636 at 23.3°/4°. These compounds gave sharp melting points at 178.0 and 215.0°K., respectively.

***o*-Xylene.**—Eastman's o-xylene (boiling range 0.2") was carefully fractionated twice in a special still. The sample employed in the specific heat determinations had an almost constant boiling point of 144.5° at 760 mm.

***m*-Xylene.**—The samples of m-xylene which we first obtained, although supposedly quite pure, melted to give a cloudy liquid and an anomalous heat absorption a few degrees above the melting point. Presumably these phenomena were due to impurities. We finally employed a sample of Kahlbaum's "purest," which we subjected to a careful fractional distillation as well as to several fractional crystallizations. It was then dried over anhydrous copper sulfate and redistilled (b. p. 139.0° at 760 mm., range less than 0.15"). This purification process apparently lowered the temperature of the heat absorption region to a point about 50° below the melting temperature and also somewhat decreased its magnitude. While the entropy value which we have obtained for *m*-xylene is probably good to within 1%, the sample was undoubtedly the least satisfactory of any employed in this investigation, as it showed considerable premelting in addition to the peculiar heat effect just mentioned.

***p*-Xylene.**—Kahlbaum's purest material was subjected to twelve fractional crystallizations. The resulting product melted sharply at 13.2'.

Diphenylmethane.—Eastman's diphenylmethane was subjected to four fractional crystallizations. The resulting product melted sharply at 25.2°.

Hexamethylbenzene, Diphenyl, **Triphenylmethane** and **Dibenzyl.**—These were relatively pure compounds, obtained from the Eastman Kodak Co. In all cases they were subjected to two or more fractional crystallizations from ethyl alcohol. The melting points of the final materials were, respectively, hexamethylbenzene 164°, diphenyl 69.1°, triphenylmethane 92.5° and dibenzyl 51.0°. They were apparently free from inorganic impurities, as samples on ignition left no residue.

Naphthalene.—Kahlbaum's naphthalene was twice crystallized from pure benzene. It was then fractionally distilled, the entire sample coming over between 217.8 and

218.0". The middle third was finally sublimed before use in the specific heat determinations.

Experimental Results

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the fusion data. The apparatus and details of experimental procedure have been fully described in other places.[6] In view of the accuracy of the various measurements involved, the error in the experimental values thereby obtained is probably less than 1%, except in so far as impurities in an hydrocarbon sample, such as that of *m*-xylene, may cause premelting or otherwise influence the results.

The specific heats and the fusion data, expressed in terms of the 15° calorie[7] and with all weights reduced to a vacuum basis, appear in Tables I and II.

TABLE I

SPECIFIC HEATS

Benzene: Crystals

Temp., °K.	92.6	97.9	103.0	113.8	129.8	143.0	150.7	162.2
C_p **per g.**	0.148	0.152	0.156	0.165	0.180	0.192	0.200	0.211
Temp., °K.	178.1	195.0	201.5	218.1	229.7	239.5	250.1	259.5
C_p **per g.**	0.229	0.250	0.260	0.283	0.301	0.317	0.335	0.355

Liquid

Temp., °K.	281.1	282.1	286.3	289.9	294.9	300.0
C_p **per g.**	0.403	0.404	0.406	0.408	0.410	0.414

Ethylbenzene: Crystals

Temp., °K.	92.7	98.0	105.5	112.6	123.1	131.1
C_p **per g.**	0.150	0.157	0.164	0.171	0.182	0.190
Temp., °K.	140.2	149.4	156.5	162.2	167.5	172.6
C_p **per g.**	0.199	0.209	0.217	0.224	0.234	0.263

Liquid

Temp., °K.	185.0	188.4	194 0	210.7	220 2	230.5	239.1	254.9
C_p **per g.**	0 352	0.354	0.356	0 364	0.368	0.372	0.377	0.385
Temp., °K.	275.3	278 4	283.0	287.9	293.0	297.4	301.2	304.9
C_p **per g.**	0.396	0.398	0.402	0.404	0.407	0.409	0.412	0.414

Tert.-butylbenzene: **Crystals**

Temp., °K.	92.2	97.9	104.2	111.6	118.2	123.2	131.0	137.9
C_p **per g.**	0.140	0.148	0.155	0.164	0.173	0.178	0.188	0.197
Temp., °K.	151.3	162.7	170.8	178.4	185.9	192.9	199.8	206.0
C_p **per g.**	0.215	0.229	0.239	0.249	0.259	0.269	0 282	0 297

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[6] Parks, THIS JOURNAL, 47, 338 (1925); also Parks and Kelley, J. Phys. Chem., 30, 47 (1926).

[7] The factor 0.2390 has been used in converting from the joule to the 15° calorie.

TABLE I *(Continued)*

Liquid

Temp., °K.	220.4	229.6	240.0	251.4	261.9	275.2	283.0	294.3
C_p per g.	0.372	0.378	0.384	0.391	0.397	0.408	0.413	0.424

o-Xylene: Crystals

Temp., °K.	90.1	93.3	96.9	109.3	123.0	136.0	148.1	161.0
C_p per g.	0.149	0.152	0.156	0.170	0.186	0.199	0.213	0.226
Temp., °K.	177.1	194.2	199.1	204.6	210.0	212.9	217.7	223.8
C_p per g.	0.242	0.261	0.270	0.283	0.314	0.287	0.293	0.302

Liquid

Temp., °K.	253.3	263.0	275.2	275.3	278.5	285.3	288.7	295.1
C_p per'g.	0.391	0.396	0.404	0.403	0.405	0.409	0.411	0.414

m-Xylene: Crystals

Temp., °K.	95.9	102.4	112.0	125.5	136.1	138.5	150.7
C_p per g.	0.160	0.165	0.174	0.186	0.195	0.197	0.208
Temp., °K.	160.8	162.0	166.1	171.0	178.6	185.3	190.2
C_p per g.	0.224	0.250	0.282	0.242	0.248	0.267	0.357

Liquid

Temp., °K.	217.0	221.1	225.0	226.9	275.0	275.3
C_p per g.	0.359	0.363	0.364	0.364	0.396	0.395

p-Xylene: Crystals

Temp., °K.	91.8	95.2	101.0	106.8	113.8	134.0	152.3	174.7
C_p per g.	0.159	0.163	0.170	0.176	0.184	0.204	0.221	0.241
Temp., °K.	184.3	205.1	225.3	245.1	255.4	266.1	276.4	280.1
C_p per g.	0.250	0.271	0.290	0.308	0.318	0.329	0.345	0.369

Liquid

Temp., °K.	290.7	292.1	294.4	299.0	299.4
C_p per g.	0.402	0.401	0.402	0.406	0.407

Hexamethylbenzene: Crystals

Temp., °K.	85.4	89.8	92.4	95.0	100.0	104.0	105.6	108.0
C_p per g.	0.155	0.164	0.170	0.176	0.190	0.248	0.342	0.50
Temp., °K.	111.8	112.6	122.4	128.8	135.6	143.0	150.7	162.9
C_p per g.	0.272	0.239	0.237	0.243	0.247	0.255	0.278	0.259
Temp., °K.	170.4	186.0	202.9	224.7	240.8	256.0	275.0	294.6
C_p per g.	0.263	0.272	0.284	0.303	0.319	0.335	0.352	0.375

Diphenyl: Crystals

Temp., °K.	93.0	98.4	105.0	113.3	134.2	152.1	173.6	183.9
C_p per g.	0.111	0.116	0.121	0.127	0.144	0.159	0.177	0.188
Temp., °K.	196.7	214.6	226.4	243.7	253.3	261.1	279.5	294.4
C_p per g.	0.199	0.217	0.229	0.246	0.255	0.264	0.283	0.301

Diphenylmethane: Crystals

Temp., °K.	89.2	93.4	99.8	107.5	122.7	129.4	136.2	150.5
C_p per g.	0.114	0.117	0.122	0.128	0.139	0.146	0.151	0.163

TABLE I (Concluded)

Temp., °K.	161.4	175.8	1851	1945	209.3	216.4	223.8	229.7
C_p per g.	0 172	0.186	0.196	0 205	0.222	0.229	0.237	0.244
Temp., °K.	236 3	242.7	251 2	267 1	268 0	275.6	282 5	
C_p per g.	0.251	0.259	0,269	0 277	0 285	0 304	0 318	

Liquid

Temp., °K.	302.0	305.4	308.7	312.3
C_p per g.	0.379	0.380	0.383	0.384

Triphenylmethane: Crystals

Temp., °K.	89.4	94.9	103.0	113.0	1221	1390	161.7	1779
C_p per g.	0103	0.108	0.114	0.121	0.128	0.141	0159	0173
Temp., °K.	196 6	202.6	229 0	238.0	248 1	275 5	283 9	294.3
C_p per g.	0.191	0.196	0.221	0 230	0 241	0 270	0 278	0 288

Dibenzyl: Crystals

Temp., °K.	92.6	99.1	107.1	115.8	1387	149.9	163.6	173.8
C_p per g.	0.125	0.129	0.136	0.143	0.161	0.170	0.182	0.191
Temp., °K.	196.2	205.5	215.1	227.6	240.4	254.3	275.0	293.6
C_p per g.	0.213	0.223	0.233	0.246	0.260	0.275	0.302	0.329

Naphthalene: Crystals

Temp., °K.	91.4	92.5	96.9	108.6	122.6	129.0	136.1	151.4
C_p per g.	0.106	0.107	0.110	0.119	0.130	0.135	0.140	0.153
Temp., °K.	171.5	186.9	202.5	224.8	254.3	275.5	283.7	295.1
C_p per g.	0.171	0.186	0.202	0.224	0.254	0.278	0.289	0.305

TABLE II

FUSION DATA[a]

Substance	M p, °K.	Heat of fusion (cal per g)		
		1st result	2nd result	Mean
Benzene	278 6	30.11	30.06	30.09
Ethylbenzene	178.0	20 63	20.62	20.63
Tert.-butylbenzene	215 0	14.96	14.93	14.95
o-Xylene	247.8	29.35	29.35	29.35
m-Xylene	219.6	25 76	...	25.76
p-Xylene	286.3	38.07	38.16	38.12
Diphenylmethane	298 3	26.36	26.40	26.38

[a] In the calculation of these fusion values, the marked rise in the specific heat of the crystals as the melting point is approached was attributed to premelting, and the heat absorbed in this region in excess of that obtained by extrapolation of the specific heat data at lower temperatures was added to the heat absorbed at the melting point.

For comparison with these values the literature contains only very meager data. Nernst[8] in his early work studied the specific heat of crystalline benzene down to the temperature of liquid hydrogen. The curve through his experimental points lies above ours by about 4.0% at 90° and 2.4% at 200°K. More recently Maass and Waldbauer,[9] using a method

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[8] Nernst, ***Ann. Physik,*** [4] 36, 422 (1911).

[9] Maass and Waldbauer, THIS JOURNAL, 47, 7 (1925).

of mixtures, have also studied benzene down to liquid-air temperatures. Their curve is quite irregular, being 11% below ours at 90°, 5% below at 150°, 6% above at 200° and 5% above at 250°K. Our curve for liquid benzene at 293°K. is less than 1% above the value selected for the "International Critical Tables."[10] In a very interesting investigation Williams and Daniels[11] have recently reported on the discovery of small irregularities in the specific heat curves of liquid benzene and ethylbenzene, which they attributed to superdrying of the liquids. We failed to observe these irregularities, possibly because our hydrocarbon samples had not been specially dried. Naturally there have been numerous determinations of the heat of fusion of benzene, the most recent values being 30.56 (Maass and Waldbauer), 29.92 (Stratton and Partington)[12] and 30.26 cal. per g. (Andrews, Lynn and Johnston).[13] The "International Critical Tables" give 30.4 cal. per g. Our mean result for benzene, 30.09, is in good agreement with all these data. The heats of fusion of *p*-xylene and diphenylmethane have also been measured before. For the former Colson[14] reported 39.3 cal. per g., which is 3.1% above our value. For the latter Tammann[15] obtained 25.3 cal. per g. or about 4.2% below our figure.

In the case of three of the hydrocarbons the specific heat curve for the crystals shows a small maximum or "hump." Such a phenomenon has been observed for several other compounds which have been studied in this Laboratory and is undoubtedly real, although its explanation is not apparent. In some instances it may be attributed to the influence of impurities in the sample, but this interpretation hardly seems valid in all cases. For o-xylene the hump comes at about 208°K. and the heat effect in excess of the normal specific heat amounts to only 0.07 cal. per g. or 7.4 cal. per mole. The two parts of the heat capacity curve below and above this transition region fit together quite smoothly, indicating that the same crystalline form probably exists over the entire temperature range. A similar but larger hump was found for m-xylene at about 166°K. and for hexamethylbenzene at 151°K. The corresponding heat effects were 0.50 and 0.23 cal. per g., respectively.

Evidence of a definite transition was also found in the case of hexamethylbenzene at about 108°K. The portions of the heat capacity curve below and above this point possess noticeably different slopes, indicative of two crystalline forms. The heat of transition as measured amounts to 1.5 cal. per g. or 250 cal. per mole.

[10] "International Critical Tables," Vol. V, p. 115.

[11] Williams and Daniels, THIS JOURNAL, 46, 1569 (1924).

[12] Stratton and Partington, *Phil. Mag.*, [6] 48, 1085 (1924).

[13] Andrews, Lynn and Johnston, THIS JOURNAL, 48, 1274 (1920)

[14] Colson, *Compt. rend.*, 104, 429 (1887).

[15] Tammann, *Göttingen Ges. Nachr.*, 335 (1913).

Discussion

Entropies of the Compounds.—Using the data contained in Tables I and II in conjunction with the third law of thermodynamics, we have calculated the molal entropies at 298.1°K. for the twelve hydrocarbons. In these calculations we have employed the extrapolation method of Kelley, Parks and Huffman[16] for estimating the entropy increases for the crystals (Col. 2 of Table III) from 0 to 90°K. The various entropy increments from 90 to 298°K., which appear in Cols. 3, 4 and 5 of the table, were obtained by the usual methods directly from the experimental data. The results for the total entropy in calories per degree appear under the heading "S_{298} experimental" in the sixth column. In the cases of the six hydrocarbons which are normally crystalline, we have roughly calculated the entropy of fusion[17] at 298° so as to obtain a value for the entropy of each compound as a liquid, even though the liquid state may be unstable at this temperature.

In the preceding paper[5] it was shown that the entropy of a liquid paraffin hydrocarbon could be calculated quite accurately by the equation, $S_{298} = 25.0 + 7.7n - 4.5r$, where n is the number of carbon atoms in the molecule and r represents the number of methyl branches on the straight chain. In the present study we have modified this equation for use with compounds containing one or more phenyl groups. It now becomes $S_{298} = 25.0 + 7.7n - 4.5r + 19.5p$, where n represents the total number of carbon atoms outside of the benzene ring and p is the number of phenyl groups in the compound. As before, r ordinarily refers to the number of methyl branches attached on the main aliphatic chain of the molecule, although in a more general sense it may be defined here as the number of hydrocarbon groups (aliphatic or aromatic), in excess of two, attached to any carbon atom in the aliphatic chain. Thus for *tert.*-butylbenzene n is 4, r is 2 and p is 1; and for triphenylmethane n is 1, r is 1 and p is 3. By this means the values of

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[16] Kelley, Parks and Huffman, *J. Phys. Chem.*, 33, 1802 (1929).

[17] This approximate calculation of the entropy of fusion was made by the equation $\Delta S_{298} = (\Delta H \text{fusion})/T_M - \Delta C_p \ln (T_M/298)$, where ΔH fusion and T_M are, respectively, the molal heat of fusion and the melting point. In all cases ΔC_p, the difference between the molal heat capacity of the liquid and crystals, was assumed to be approximately 0.05 cal. times the molecular weight. For diphenyl, dibenzyl and naphthalene we have taken the values of the heat of fusion as given in the "International Critical Tables" (Vol. V, p. 132). For triphenylmethane the value obtained by Hildebrand, Duschak, Foster and Beebe [THIS JOURNAL, 39, 2293 (1917)] appears to us to be too low, owing to an inadequate allowance for premelting of the sample; and from a study of the published data we have somewhat arbitrarily increased their result to 20 cal. per g. In the absence of any data for the heat of fusion of hexamethylbenzene, we have assumed a molal entropy of fusion of 19.0 E. U. at the melting point, 437°K. This value was obtained by taking the average entropy of fusion of the xylenes, 13.0 E. U. per mole, and adding thereto 1.5 E. U. for each additional CH_3 group in the hexamethylbenzene molecule. The result is probably accurate to within 10%.

"S_{298} predicted" in the last column of Table III were obtained for all the substances except naphthalene. It will be observed that the agreement between the experimental and predicted values is very good[18] except for two compounds—benzene and diphenyl.

TABLE III

ENTROPIES OF THE HYDROCARBONS PER MOLE

Substance	Crystals 0–90°K.	Crystals Above 90°K.	Fusion	Liquid	S_{298} experi-mental	Sass predicted
Benzene	11.35	20.00	8.43	2.15	41.9	44.5
Ethylbenzene	14.60	13.66	12.30	20.60	61.2	59.9
Tert.-butylbenzene	16.18	23.94	9.32	17.20	66.6	66.3
o-Xylene	14.53	23.96"	12.57	8.12	59.3	59.9
m-Xylene	16.00	19.40^b	12.45	12.42	60.3	59.9
p-Xylene	15.58	29.06	14.13	1.71	60.5	59.9
Hexamethylbenzene (solid)	19.69	54.30^c	..	...	74.0	..
Hexamethylbenzene (liquid)			15.9	...	89.9	90.7
Diphenyl (solid)	15.63	33.52	..	...	49.2	..
Diphenyl (liquid)			10.6	...	59.8	64.0
Diphenylmethane (solid)	18.61	38.64	..	...	57.2	..
Diphenylmethane (liquid)			14.86	...	72.1	71.7
Triphenylmethane (solid)	23.84	50.78	..	...	74.6	..
Triphenylmethane (liquid)			10 9	...	85.5	86.7
Dibenzyl (solid)	21.60	43.00	..	...	6 4 6	..
Dibenzyl (liquid)			16 6	...	81.2	79.4
Naphthalene (solid)	12.69	27.21	..	...	39.9	..
Naphthalene (liquid)			11.8	...	51.7	..

[a] This value includes 0.04 E. U. for the entropy of the hump at 208°K. [b] This value includes 0.30 E. U. for the entropy of a hump at 166°K. [c] This value includes 2.28 E. U. for the transition at 108° and 0.24 E. U. for the entropy of a hump at 151°K.

In the case of benzene there is a discrepancy of 2.6 E. U. or about 6%, which is undoubtedly due to the fact that this substance is somewhat unique in character. For diphenyl the discrepancy is about 7% and is largely due to a relatively low value for the entropy of fusion. This at once suggests that the experimental result for the heat of fusion of this compound may be too low, a question on which we hope soon to obtain further information through some new experimental work.

In the preceding study the entropy of *n*-hexane was found to be 71.1 E. U.; that for n-decane can be predicted to be about 102 E. U. Thus, compared with saturated aliphatic compounds of the same number of carbon atoms, the entropies of liquid benzene and naphthalene at 298°K. are very small. As S_{298} for cyclohexane was found to be 49.2 E. U., it is evident that this difference is primarily due to the ring structures of benzene and naph-

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[18] This empirical equation also gives a good check in the case of the entropy of toluene. Using it, we calculate the value of 52.2 E. U. per mole; while Kelley [THIS JOURNAL, 51, 2740 (1929)] has recently obtained 52.4 E. U. in an experimental investigation

thalene rather than to unsaturation in the molecule or to the withdrawal of hydrogen.

The Free Energies of the Hydrocarbons

We have also calculated the free energies of these twelve hydrocarbons by means of the third law of thermodynamics and the fundamental thermodyanmic equation, A F = A H − TAS.

The essential data are given in Table IV. For obtaining the figures for the A H of formation of the first six compounds we have used the heats of combustion determined by Richards and his co-workers, and more recently revised by Swietoslawski and Bobinska.[19] This procedure has seemed desirable, both because of the known excellence of Richards' work and the fact that all these data are then on a comparative basis. For the remaining six compounds we have taken the heats of combustion as given in the "International Critical Tables."[20] Except for naphthalene, these last values depend almost entirely upon Stohmann's determinations, which recent studies[21] have shown may be in error by 0.5% in some instances. For our present purpose we have converted all the combustion data to 298.1°K. The ΔH_{298} values were then calculated by use of 68,330 and 94,270 cal.[5] for the heats of combustion of hydrogen and graphitic carbon, respectively. Column 4 contains the entropy of formation of each compound, which is simply the difference between its S_{298} and the corresponding values for the entropies of the elements contained therein. For this purpose the respec-

TABLE IV

THERMAL DATA AT 298.1°K.

The 15° cal. is used throughout and all weights have been reduced to a vacuum basis

Substance	Heat of combustion at constant *pressure*	ΔH_{298}, cal.	ΔS_{298}, E. U.	ΔF°_{298}, cal.
Benzene	782,000	+11,300	− 54.7	+ 27,600
Ethylbenzene	1,090,400	− 5,400	− 97.2	+ 23,600
Tert.-butylbenzene	1,400,400	−20,700	−153.6	+ 25,100
o-Xylene	1,090,800	− 5,000	− 99.1	+ 24,500
m-Xylene	1,090,800	− 5,000	− 98.1	+ 24,200
p-Xylene	1,087,000	− 8,800	− 97.9	+ 20,400
Hexamethylbenzene (S)	1,711,400	−34,900	−208.0	+ 27,100
Diphenyl (S)	1,493,300	+20,400	−114.4	+ 54,500
Diphenylmethane (S)	1,654,700	+19,200	−137.3	+ 60,100
Triphenylmethane (S)	2,383,500	+45,700	−186.9	+101,400
Dibenzyl (S)	1,810,200	+12,100	−160.8	+ 60,100
Naphthalene (S)	1,231,600	+15,600	− 91 5	+ 42,900

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[19] Swietoslawski and Bobinska, THIS JOURNAL, 49, 2478 (1927). The values have been increased by 0.017%, as suggested by Verkade and Coops [*Rec.* trav. *chim.*, 46, 910 (1927)].

[20] "International Critical Tables," Vol. V, p. 163.

[21] Verkade and Coops, *Rec. trav. chim.*, 47,608 (1928).

tive entropies of carbon and hydrogen were taken as 1.3 and 14.8 E. U.5 per gram atom.

The molal free energies appear in the last column of the table. For comparative purposes the accuracy of these values is largely limited by the accuracy of the combustion data employed. In the case of the first five compounds and naphthalene the combustion values are probably good to within a thousand calories. For the other substances, the errors may be greater, depending somewhat upon the magnitude of the heat of combustion involved. Thus the result for triphenylmethane may be uncertain to the extent of, perhaps, ten thousand calories. In a consideration of the table it also should be noted that the results for the last six compounds refer to the solid state. However, the free energy value for liquid diphenylmethane at 298.1°K. is practically identical with that for the crystalline material, since the melting point is only slightly above this temperature. In the case of the other five compounds the differences between the liquid and solid states at 298°K. can be calculated roughly (*i.e.*, to 10% or better) by the equation, $\Delta F_{298} = \Delta S_{\text{fusion}} (T_m - 298.1)$. By this means we estimate that the free energy of liquid hexamethylbenzene exceeds that of the solid by 2700 cal. In the cases of diphenyl, triphenylmethane, dibenzyl and naphthalene, the differences are 500, 800, 500 and 600 cal., respectively.

In spite of the purely qualitative character of some of the free energy data in Table IV, two interesting points are worthy of brief attention. First, the introduction of a phenyl radical into a saturated aliphatic hydrocarbon raises the free energy level by about 35,000 cal. Thus the free energy of liquid methane at 298°K. has been estimated as —9800 cal.[22] and on this basis that of toluene should be about +25,200 cal., a value which is in good agreement with the result (+24,300 cal.) recently obtained by Kelley.[23] Similarly, we can predict the values +60,200, +60,800 and +95,200 cal. for diphenylmethane, dibenzyl and triphenylmethane, respectively, all in the liquid state at 298°K. These predicted quantities differ by 100, 200 and 7000 cal. from the corresponding experimental ones.

The second feature concerns the relations of benzene and its derivatives. It is apparent that the free energy level of benzene itself is somewhat above that for the simple mono- and disubstitution products. On the other hand, with the single exception of *p*-xylene, all these simple derivatives—toluene, ethylbenzene and the xylenes—have the same free energies within a thousand calories. Furthermore, it is possible that the discrepancy of over 3000 cal. in the case of *p*-xylene is partly due to an error in Richards' heat of combustion of this compound, since other investigators in thermochemistry have obtained almost identical values[24] in the case of such iso-

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[22] Parks and Kelley, THIS JOURNAL, 47, 2096 (1925).

[23] Kelley, *ibid.*, 51, 2740 (1929).

[24] See, for instance, Keffler and Guthrie, *J. Phys. Chem.*, 31, 65 (1927).

mers. We, therefore, are inclined to agree with Andrews' conclusion that ortho, meta and para isomers have practically identical free energies of formation.[25] With the introduction of more methyl groups into the benzene ring, the free energy probably rises slightly, as our value of +29,800 cal. for hexamethylbenzene in the liquid state indicates.

The Free Energy Change in the Hydrogenation of Benzene.—The data now available permit us to study by two different methods the free energy change for the hydrogenation reaction: $C_6H_6(l) + 3H_2(g) = C_6H_{12}(l)$.

The equilibria between benzene, hydrogen and cyclohexane have been measured at 266.5 and 280° by Burrows and Lucarini.[26] From their results Francis[2'] has obtained the equation $A F = -46,800 + 19.75\ T \ln T - 0.0115\ T^2 - 34.5\ T$ for the reaction in the gaseous phase. This equation, however, was derived by the use of Richards' value for the heat of combustion of benzene and that of Zubow, as revised by Swietoslawski, for cyclohexane. It is highly questionable whether Zubow was able to secure complete burning of such a volatile material. Moreover, as the heats of combustion of both substances have been determined by Richards and his co-workers and by Roth and von Auwers, we feel that it is preferable to rely solely upon the work of these two groups of investigators in a calculation of this kind. Using Richards' data,[19] we obtain $\Delta H_{293} = -47,000$ cal.; Roth's results[28] give $\Delta H_{291} = -48,800$ cal. As a mean we have $\Delta H_{292} = -47,900$ cal., as against the figure $\Delta H_{293} = -51,600$ cal., employed by Francis. This value applies to the above reaction involving benzene and cyclohexane as liquids. For the reaction in the gaseous phase we obtain $\Delta H_{292} = -48,100$ cal., since the molal heat of vaporization of benzene exceeds that of cyclohexane by about 200 cal.[29] The preceding free energy equation must then be modified and we find that $A F = -43,300 + 19.75\ T \ln T - 0.0115\ T^2 - 41.1\ T$. Then at 298°K., $A F = -23,030$ cal. This result is for the process at 1 atm. in the gaseous phase, but the free energy change when benzene and cyclohexane are in the liquid state will be the same, as the vapor pressures of these compounds are practically equal.

The entropy data now enable us to obtain a second result. From the ΔH_{292} value in the preceding paragraph and -16 cal. for ΔC_p we calculate $\Delta H_{298} = -48,000$ cal. for the reaction involving the liquids. Also $\Delta S_{298} = 49.2^5 - (41.9 + 88.8) = -81.5$ E. U. Hence, it follows that $\Delta F_{298} = -48,000 + (298.1)(81.5) = -23,690$ cal. Thus these two free energy changes, obtained by very different experimental methods, differ by 660 cal. or about 2.8%.

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[25] Andrews, **This Journal**, 48, 1296 (1926).

[26] Burrows and Lucarini, *ibid.*, 49, 1157 (1927).

[27] Francis, *Ind. Eng. Chem.*, 19, 277 (1928).

[28] Landolt, Bornstein, Roth, Scheel, "Tabellen," 1923, p. 1589

[29] Ref. 28, p. 1483.

Summary

1. The specific heats of twelve aromatic hydrocarbons have been measured over a wide range of temperatures. The heats of fusion of seven of these compounds have also been determined.

2. The entropies of the twelve hydrocarbons have been calculated from these heat capacity data. The results thus obtained have been found to agree in most cases with the values predicted by means of a simple, empirical equation.

3. The corresponding free energies have also been calculated and certain regularities noted. The free energy change in the hydrogenation of benzene to give cyclohexane has been derived in two different ways.

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[CONTRIBUTION FROM UNIVERSITY COLLEGE, THE UNIVERSITY OF LONDON]

THE ACTION OF DIAZOMETHANE ON BENZOIC AND SUCCINIC ANHYDRIDES, AND A REPLY TO MALKIN AND NIERENSTEIN

BY W. BRADLEY AND R. ROBINSON

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The memoir by Malkin and Nierenstein[1] contains some statements requiring comment.

(1) The Course of the Interaction of Diazomethane and Acid Chlorides.—The implication of these authors that the merit of experiments on the interaction of benzoyl chloride and diazomethane is directly proportional to the yield of ω-chloro-acetophenone obtained is quite unwarranted. In our work, for example, we were not trying to obtain the chloro-ketone, but rather to isolate the first stage and product of the reaction, and, with this end in view, we operated at a low temperature and, for reasons that appear in the sequel, kept the diazomethane in excess.[2] Under these circumstances benzoyl chloride is rapidly and completely transformed into diazo-acetophenone, and evolution of nitrogen is evident.

Therefore, we have the reaction

$$C_6H_5COCl + CH_2N_2 = C_6H_5COCHN_2 + HCl \qquad (I)$$

The resulting hydrogen chloride, reacting with the diazomethane in excess, must then give methyl chloride and nitrogen

$$CH_2N_2 + HCl = CH_3Cl + N_2 \qquad (II)$$

Thus when benzoyl chloride (1 mole) is added to a cold ethereal solution of diazomethane (2 moles), the reaction is undoubtedly represented by the equation

$$C_6H_5COCl + 2CH_2N_2 = C_6H_5COCHN_2 + CH_3Cl + N_2 \qquad (III)$$

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[1] Malkin and Nierenstein, THIS JOURNAL, 52,1504 (1930).

[2] Bradley and Robinson, J. Chem. *Soc.*, 1317 (1928).

We think this so obvious that experimental confirmation of the formation of methyl chloride is unnecessary; nevertheless, it is hoped to remedy the omission in the near future.

We must further point out that our view of the course of the reaction is based on this ready formation of an almost quantitative yield of diazo-acetophenone, and *not* on Experiment V of Bradley and Schwarzenbach,[3] to which Malkin and Nierenstein attribute an importance not claimed in the original. This and analogous experiments must be carried out accurately under various conditions before the discussion can be profitably continued. Nevertheless, it should be stated at once that the volume of nitrogen at N. T. P. theoretically obtainable from the diazomethane used by Bradley and Schwarzenbach is 1355 cc. as originally computed, and not 1772 cc. as now corrected, albeit erroneously, by Malkin and Nierenstein.

Equations I and II are summarized in III, but, if the concentration and total quantity of diazomethane is diminished, then, clearly, the less reactive diazo-acetophenone may be decomposed by accumulated hydrogen chloride

$$C_6H_5COCHN_2 + HCl = C_6H_5COCH_2Cl + N_2 \qquad (IV)$$

Equations I and IV are summarized by the following

$$C_6H_5COCl + CH_2N_2 = C_6H_5COCH_2Cl + N_2 \qquad (V)$$

On the basis of this theory, it is easy to devise a process which will give the maximum yield of w-chloro-acetophenone. In the first place, the total amount of diazomethane used should be restricted to the minimum requisite, and it should be slowly added to a solution of the acid chloride. In this way Reaction I should occur and II should be avoided, since diazomethane is not present in significant concentration. Time must be allowed for the occurrence of IV, after which more diazomethane may be introduced. It is not surprising that, under such conditions, the net result may be represented by V. An elevated temperature, by increasing the velocity of the reactions, will shorten the time expended and allow of a relatively more rapid introduction of the diazomethane. We cannot agree that the course of the reaction is fundamentally different at 0 and at 18°. Thus the experiments of Malkin and Nierenstein, in which these requirements are fulfilled, afford strong support to our view of the mechanism of the reaction.

The sole existing evidence opposed to our hypothesis, and favoring the view of Malkin and Nierenstein that an addition compound of acid chloride and diazomethane breaks down directly into chloro-ketone and nitrogen, is furnished by the formation of the diaryldihalogenodioxanes of Lewis, Nierenstein and Rich,[4] which, however, we have not been able to obtain. Naturally, we agree that a loose additive complex must be formed in the first phase of the reaction even on our hypothesis, and this view we have

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[3] Bradley and Schwarzenbach, J. Chem. *Soc.,* 2904 (1928).

[4] Lewis, Nierenstein and Rich, THIS JOURNAL, 47, 1728 (1925).

already embodied in a discussion of the reaction on an electronic basis, using Langmuir's translation of the Thiele formula.[2,5]

(2) The Constitution of Diazo-acetophenone.—Our statement that diazo-acetophenone was decomposed by iodine in cold alcoholic solution was based on a test-tube experiment. If a few crystals of iodine are added to a cold, concentrated alcoholic solution of the diazo-ketone, there is an immediate evolution of nitrogen, accompanied by a rise of temperature. Heat could not be produced unless the reaction started in the cold, and, in any case, the experiment was sufficient for our purpose, which was to show the analogy of diazo-acetophenone with other diazo compounds. The reaction seems to go better in methyl than in ethyl alcohol, and proceeds slowly in cold, dilute, alcoholic, ethereal or chloroform solutions. Diazo-acetophenone is quickly decomposed by cold solutions of hydrogen chloride, and it is, therefore, very unlikely that it possesses a full diazo-anhydride structure, as suggested by Malkin and Nierenstein. True diazo-anhydrides have been considered to be represented by such substances as diazo-benzoylacetone and ethyl diazo-acetoacetate, and these are very much more stable than is diazo-acetophenone toward hydrochloric acid and iodine. For example, Wolff[6] stated that diazobenzoylacetone was soluble in cold, concentrated hydrochloric acid and was recovered unchanged on the addition of water. Similarly, ethyl diazo-acetoacetate was not attacked by iodine in hot chloroform solution.

The stabilizing effect of the carbonyl group on the diazo center in diazo-acetophenone is but one manifestation of a very general phenomenon; another example is found in ethyl diazoacetate. The relative resistance to the action of cationoid reagents, such as acids and halogens, varies from case to case, and is entirely in agreement with the hypothesis that such resistance is increased by the proximity of electron-attracting (cationoid) groups in the molecule. Such centers, by virtue of the positive field which they produce, quite naturally hinder the attack of cations or electron-seeking agents generally. We consider it very probable that there is a weak but definite *electrovalency* established between the oxygen of the carbonyl and the diazo group, either directly or through the medium of polar centers in the surroundings. The value of the poles on this *betaine* theory will depend on the constitutive factors; the substances, in fact, are probably anhydronium bases (Armit and Robinson),[7] intermediate in constitution between the keto-diazo and enol-diazonium-betaine forms, and even the reputed true diazo-anhydrides may be accommodated in this scheme.

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[5] The formulation suggested and preferred by W. A. Noyes affords an equally satisfactory basis of discussion and this is also true of the cyclic formula, recently revived by Sidgwick.

[6] Wolff, *Ann.,* 325, 129 (1902)

[7] Armit and Robinson, J. *Chem. Soc.,* 127, 1604 (1925).

On the basis of the above suggestions, it is possible to arrange the aliphatic diazo compounds in a predicted order of stability toward cationoid agents. Placing the more reactive substances first, this should be: 2-diazopropane, diazoethane, diazomethane, phenyldiazomethane, ethyl α-diazopropionate, ethyl diazoacetate, diazo-acetone (in derivatives, substitution by alkyl should increase reactivity, and by halogen decrease reactivity, subject to influences of a steric nature in highly substituted compounds), diazophenylacetone, diazo-acetophenone (alkylated, more reactive, halogenated, carbethoxylated, and especially nitro derivatives, less reactive), diazo derivatives of aliphatic β-ketonic esters, diazo derivatives of aromatic β-ketonic esters, diazo derivatives of diketones (aliphatic and alkylated, more reactive; aromatic and nitroxylated, less reactive).

(3) The Practical **Aspect.**—Clibbens and Nierenstein[8] gave very sparse details of their experimental procedure, so that it was quite possible to repeat their experiments and obtain divergent results. Neither the temperature nor the scale of the operations was specified, and the rate of addition of the diazomethane, the most vital detail, was not mentioned. We agree, of course, that, when a temperature is not indicated, the ordinary temperature is implied, but, for our own part, cooling in ice water is also a normal procedure in manipulating solutions of diazomethane.

We have made no direct criticism of the memoir of Clibbens and Nierenstein, other than that involved in the contrast with our own results; this divergence has been satisfactorily explained by the disclosure of further details of the original preparations.

Unfortunately, we cannot attempt to confirm later experiments of Nierenstein,[9] the results of which are not in harmony with our views, because the preparation of the starting point—namely, 3,4,2′,4′,6′-pentamethoxydiphenylacetic acid—could not be repeated by one of us (R. R.), despite several attempts at intervals. The great importance of the reaction in synthetic work makes it desirable to add that, if a chloro-ketone is the object aimed at, then diazomethane should be led into a solution of the acid chloride until the former is present in excess after a short interval; any diazo-ketone should then be decomposed by the introduction of hydrogen chloride. In all other cases it is best to proceed through the diazo-ketone, and the acid chloride is then added to two or more molecular proportions of diazomethane.

(4) The Historical Aspect.—Nierenstein and his collaborators, working with acid chlorides and diazomethane over a long period, never observed the formation of the diazo-ketones, although the chlornitraldin of Dale and Nierenstein[10] may have been w-diazo-o-nitro-acetophenone. The recogni-

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[8] Clibbens and Nierenstein, J. Chem. *Soc.*, 107, 1491 (1915).

[9] Nierenstein, *ibid.*, 117, 1153 (1920).

[10] Dale and Nierenstein, Ber., 60, 1026 (1927).

tion that the product of the action of diazomethane on o-nitrobenzoyl chloride has this constitution is due to Arndt, Eistert and Partale.[11]

This single instance escaped the attention of the present authors, who encountered another case in connection with work on the synthesis of malvidin Memoirs on the interaction of benzoyl chloride and diazomethane were then published simultaneously by Arndt and Amende, and by the present authors. We have already taken an opportunity to admit the priority of Arndt, established by the diazo-o-nitro-acetophenone case, but the fact that we made the discovery of the formation of the diazoketones independently could not be gathered from a perusal of the references given by Malkin and Nierenstein.

(5) A short experimental section is appended, in which it is shown that diazomethane reacts with benzoic anhydride, forming methyl benzoate and diazo-acetophenone.

$$C_6H_5COOCOC_6H_5 + 2CH_2N_2 = C_6H_5CO_2CH_3 + C_6H_5COCHN_2 + N_2$$

Using succinic anhydride and normally dried reagents, we could isolate nothing but methyl succinate. With exceptional precautions for the exclusion of water and alcohols, the products were methyl succinate, a diazo derivative and other unidentified compounds. The formation of methyl succinate was not found to depend on the preliminary hydrolysis to succinic acid, and evidently succinic anhydride and diazomethane give a complex which is quite abnormally reactive toward water or one of the simple alcohols.

Related observations have already been recorded. Herzig and Tichatshek[12] noticed that m-acetoxybenzoic acid gave with diazomethane in not quite anhydrous neutral media an 88% yield of *m*-methoxybenzoic acid (after hydrolysis of the ester) in forty-eight hours. It is difficult to believe that this is the result of consecutive hydrolysis and methylation, although this is the view put forward by Herzig and Tichatshek.

Again, Meerwein and Burneleit[13] found that diazomethane does not react with cold acetone and only slowly with water and the simple alcohols. Nevertheless, a vigorous evolution of nitrogen occurs when the gas is led into acetone containing 10–15% of water. The main product is then asymmetric-dimethylethylene oxide, but isobutyraldehyde and methyl ethyl ketone are also formed. Arndt and collaborators have observed and discussed other cases of a similar kind.

Experimental

Benzoic Anhydride and Diazomethane.—Benzoic anhydride (1 mol., 4.5 g.), dissolved in ether (20 c~.) cooled to 0°, was added in one portion to ethereal diazomethane

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[11] Arndt, Eistert and Partale, Ber., 60, **1364** (1927).

[12] Herzig and Tichatshek, *ibid.,* 39, 1558 (1906).

[13] Meerwein and Burneleit, *ibid.,* 61, 1841 (1928).

(from 10.5 cc. of nitrosomethylurethan, 2.5 mols of CH_2N_2) at −5°. There was no immediate evolution of nitrogen, and none was observed on occasional inspection during three days, on the first two of which the solution was cooled in ice water. During the third day, the flask was allowed to reach the room temperature and the product was isolated by removal of the solvent in a current of dry air. The residual yellow oil was taken up in light petroleum and, on cooling in ice, pale yellow crystals (1.25 g., m. p. 42–44°) separated. The substance had all the properties of diazo-acetophenone (m. p. 4848.5°), and, on recrystallization, separated as flat, pale yellow needles, m. p. 47–48°. Nitrogen was estimated by decomposition with 20% hydrochloric acid. (Found: diazo nitrogen, 19.0, 19.0. Calcd. for $C_8H_6ON_2$: N, 19.2.) Further crops of less pure material separated on evaporation of the mother liquor and, after complete removal of the solvent, the oil was distilled. The boiling point rose quickly to 195° and 1.4 g. of colorless methyl benzoate (b. p., 198°) was collected at 195–197°. There was only a small, dark brown residue in the flask,

Succinic Anhydride and **Diazomethane.**—The succinic anhydride employed was crystallized from ethyl acetate, and had m. p. 118–119° (literature, 118').

EXPERIMENT I.—Diazomethane (2.5 mols) from 50 cc. of nitrosomethylurethan was distilled into finely powdered succinic anhydride (9.0 g.) suspended in a little dry ether and cooled to −10°. There was no visible evolution of nitrogen but, despite the extremely sparing solubility of the anhydride in cold ether, the whole of the material passed into solution within three days, during the first two of which the reaction mixture was kept in ice, and, later, at the room temperature. The solution was evaporated in a current of dry air and the bright yellow oil which remained was dissolved in dry ether (25–30 cc.) and filtered from a small, insoluble residue (0.6 g.). When cooled in an ice–salt freezing mixture during thirty minutes, only a very small amount of a flocculent substance separated from the filtrate; the absence of unchanged succinic anhydride was thus assured.

For purposes of calculation, the filtrate was diluted to 90 cc. with dry ether, and portions of the solution (Y—10 cc. corresponded to 1 g. of succinic anhydride) were examined as follows.

(a) Ten cc. of Y was evaporated as completely as possible in a current of dry air. The residue weighed 1.2104 g. (X). This product gave very readily all the common reactions of diazo compounds. It was a bright yellow, mobile oil, from which nitrogen was evolved on heating or keeping. The same decomposition was effected by iodine, mineral acids and glacial acetic acid; the product reduced Fehling's solution. The alcoholic solution gave with a drop of aqueous sodium hydroxide a yellow color; this became red immediately on warming. Quantitatively, however, the matter assumed a different aspect (found in X: diazo nitrogen, 0.6%).

A specimen (Z), prepared and isolated in a similar manner, but kept in a vacuum over sulfuric acid, decreased continuously in weight during two weeks. In the meantime the color changed from pale yellow to light orange. (Found in Z: diazo nitrogen, 0.37%, and N by Dumas, N, 1.85%.)

(b) Seventy cc. of the ethereal solution (Y) was evaporated on the water-bath and the residual oil distilled from a glycerol bath in a current of dry carbon dioxide. The oil passed over almost completely at 90–92° (14 mm.), leaving only a small brown residue; it was colorless (yield, 7.43 g.) and had a slight basic odor. Redistilled, the oil boiled constantly at 91–92' (14 mm.), and solidified in contact with ice within a few minutes to a crystalline mass of stout prisms, m. p. 18–19'. On heating with hydriodic acid under Zeisel conditions, methyl iodide was formed at below 60°. (Found: CH_3O, 42.0, 42.0. Calcd. for $C_4H_4O_2(OCH_3)_2$, CH_3O, 42.5%.) Dimethyl succinate has m. p. 19° (18.5°); b. p. 80° (10–11 mm.) and 195.3° (corr.). Calculated for the original *g*. of succinic anhydride, the yield of dimethyl succinate is 9.55 *g*., or 72.7% of the theoretical.

EXPERIMENT 11.—Experiment I was repeated with the following modifications. Succinic anhydride (4.5 g.) and nitrosomethylurethan (25 cc.) were used. The methyl alcoholic potassium hydroxide was replaced by absolute n-butyl alcoholic potassium hydroxide. The access of moisture was completely prevented. The amount of diazomethane consumed was estimated.

Ether, already dried by phosphoric anhydride, was treated with sodium wire during three days and then redistilled over phosphoric anhydride. Toward the end of the diazomethane preparation, it was necessary to raise the temperature of the generating flask to 50–60°, in order to prevent the separation of solid matter which interfered with the diffusion of the alcoholic potash.

When the distillation was complete, about 15 cc. of the ethereal distillate, after being well mixed and allowed to settle, was decanted into a small, dry flask, and this was kept under the same conditions as the main portion (135 cc.), which contained finely powdered succinic anhydride (4.5 g.) in suspension. Contact of the solution with the atmosphere was reduced to a minimum by sealing the flasks with wax and inserting a capillary mercury seal between the flask and the usual calcium chloride tube. The reactants were kept at 0° during one day, and subsequently at the room temperature.

The rate of dissolution of the anhydride was markedly less rapid than under the conditions of Experiment I, and this was probably not the result of difference in the state of subdivision of the finely powdered anhydride. After three days the diazomethane content of the 15-cc. ethereal solution was determined, and after six days that of the main 135-cc. portion. In each estimation ethereal diazomethane solution was added to excess of benzoic acid dissolved in ether, and the excess estimated by titration with 0.1 N sodium hydroxide after dilution with much aqueous alcohol. The 15-cc. solution contained 0.0250 g. of CH_2N_2/cc., and the 135-cc. solution contained 0.00645 g. of CH_2N_2/cc.

After six days a considerable amount of solid remained undissolved; this was collected and dried (1.72 g., m. p. 115–118°—a trace persists to 122°). It was, presumably, unchanged anhydride (m. p.. 117–118°). The filtrate was evaporated in a current of dry air, and the diazo nitrogen content of the residue—a deep yellow oil, which lost nitrogen on keeping during a few hours—determined. (Found: diazo nitrogen, 2.4%.)

The remainder of the oil was distilled from a glycerine-bath in a current of carbon dioxide. Unlike the product of Experiment I, it was far from homogeneous; a colorless oil passed over at 87–103° (17 mm.), and a dark brown, oily residue remained which did not distil below 150° (17 mm.). The residue formed about one-half of the product. The distillate solidified to a colorless, well crystallized mass when cooled in ice. This had m. p. 19" and was found to consist of methyl succinate by comparison with an authentic sample.

The amount of diazomethane which reacts with a given weight of the anhydride is not precisely known, since decomposition of the diazomethane is proceeding simultaneously with the fall in concentration due to reaction with the anhydride, and the rate of decomposition is probably itself a function of the concentration. If, however, the concentration after three days is a fair average, then the data show that the molecular reacting ratio, diazomethane/anhydride, is approximately 2 (actually, 2.15).

Summary

1. Since diazomethane and benzoyl chloride react at 0° with great facility to yield diazo-acetophenone, this substance is regarded as the pri-

mary product of the reaction. The validity of the categorical summary of Malkin and Nierenstein's paper is questioned.

2. It is suggested that the formation of ω-chloro-acetophenone is a secondary process and the result of the action of hydrogen chloride on diazo-acetophenone. The special conditions prescribed by Malkin and Nierenstein are such as to favor this secondary process.

·3. The interaction of benzoic and succinic anhydrides with diazomethane has been studied. The formation of methyl succinate in the latter case occurs in the presence of water (or methyl alcohol), but, in all probability, succinic acid (or methyl hydrogen succinate) is not an intermediate in the process.

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VAPOR PHASE ESTERIFICATION OF ACETIC ACID BY ETHYL ALCOHOL

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The object of this work was to determine the equilibrium concentration of ethyl acetate in the vapor phase esterification of ethyl alcohol by acetic acid according to the reaction

$$C_2H_5OH + CH_3COOH = CH_3COOC_2H_5 + H_2O$$

Of the various esterification reactions this is the one which has been most frequently studied in the vapor phase, but there does not appear to be any consistency in the values of the equilibrium constant reported in the literature. From experiments with zirconium oxide as the catalyst Mailhe and de Godon[1] concluded that the equilibrium constant was about 6.0 in the temperature range of 280–290°. Mulliken, Chappell and Reid,[2] in studying the formation of ethyl acetate in the presence of silica gel, obtained results which gave an equilibrium constant of 79.3 at 150°, although they believed the actual value to be considerably higher. These experimenters also observed a considerable variation in the equilibrium constant with temperature. By determining the composition of the vapor above a liquid equilibrium mixture of alcohol, acid, ester and water, Edgar and Schuyler[3] obtained values of the equilibrium constant varying between 347 and 559 for the vapor phase in a temperature range of 72.6 to 77.6°, admitting the possibility of a considerable error. Recently

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[1] Mailhe and de Godon, *Bull. soc. chim.*, **29**, 101 (1921).

[2] Mulliken, Chappell and Reid, *J. Phys. Chem.*, **28**, 872 (1924).

[3] Edgar and Schuyler, This Journal, 46, 64 (1924).

Swietoslawski and Poznanski,[4] using the same method but claiming a greater degree of accuracy, reported a value of 59.0. In no case has the equilibrium been approached from the ester–water side, however.

Since these values of the equilibrium constant correspond to conversions of from 71 to 95% for mixtures of ethyl alcohol and acetic acid in equimolal concentrations over a range of 74 to 290° without, however, showing a definite trend in the effect of temperature, an attempt was made to redetermine the equilibrium under carefully controlled conditions. To this end experiments were made in which the equilibrium was approached from both sides over a temperature range of 250 to 300°. On the basis of Mailhe's data zirconium oxide was chosen as the catalyst possessing the highest activity without giving rise to side reactions at the temperatures in question.

Experimental Procedure

The apparatus consisted of two concentric coils of pyrex tubing connected in series and immersed in a fused salt-bath containing equal amounts of sodium and potassium nitrate. The bath was electrically heated and its temperature could be maintained constant within ±0.5°. The inner coil served as a vaporizer and preheater while the outer and larger coil contained 50 cc. of catalyst consisting of 5 g. of zirconium oxide supported on granulated pumice. In the esterification experiments a mixture of glacial acetic acid and anhydrous ethyl alcohol was passed from a buret at a fixed rate into the preheater coil. Since the ester and water were immiscible in the proportions used it was necessary in the hydrolysis experiments to feed the two liquids into the preheater in separate streams. The vapors issuing from the reactor were passed through a condenser and collected in an ice-cooled receiver. The acid content of the product was determined by titration and the equilibrium constant calculated from the percentage conversion. To determine the extent of olefin formation, gas samples were collected at the higher temperatures, *i. e.*, above 300°.

The catalyst was prepared by precipitating zirconium oxide with ammonia from a nitrate solution containing suspended pumice. The resulting material was dried in an electric oven at 90° and subsequently heated in the reactor for several hours at 280° in order to dehydrate the zirconium hydroxide and remove occluded ammonium salts.

Discussion of Results

The results of esterification experiments made with equimolar mixtures of acetic acid and ethyl alcohol at 250, 280 and 300° are listed in Table I. For each temperature the percentage conversion into ethyl acetate is given, together with the feed rate expressed as the number of cc. of liquid entering per hour per 100 cc. of catalyst. In Fig. 1 the conversions at 250 and 280° are plotted against the inverse of this rate. The curve for 280° shows that as the velocity of the vapor over the catalyst decreases, the percentage conversion into ethyl acetate increases rapidly at first, then more and more slowly, until finally it reaches the equilibrium value in the usual asymptotic manner. The average conversion calculated

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[4] Swietoslawski and Poznanski, *Roczniki Chem.*, 8, 527 (1928); C. A., 23, 2093 (1929).

from the six points on the flat portion of the curve is 87.5%, corresponding to a value of 49.0 for the equilibrium constant of the reaction. At lower temperatures it becomes necessary to correct for the polymerization of acetic acid into double molecules, as pointed out by Edgar and Schuyler.[3] However, extrapolation of Drucker and Ullmann's data[5] gives an equilibrium constant of 0.00437 at 280°, corresponding to only 1% polymerization of the acid. In addition to being somewhat uncertain, the corresponding correction is, therefore, too small to be considered in calculating the equilibrium constant for the esterification reaction at these temperatures.

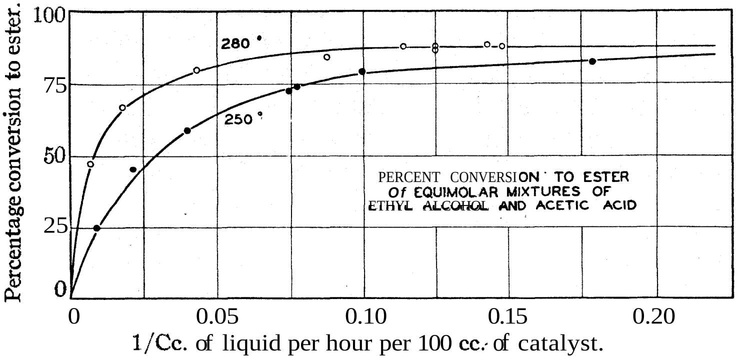

Fig. 1.

At 250° the reaction velocity is so slow that the equilibrium concentration is not reached even at the longest time of contact employed, as seen from the lower curve in Fig. 1. The results obtained at 300°, on the other hand, fall closely along the curve for 280° and for clarity have been omitted from the diagram. The average of the last five experiments at 300°, taken from Table I, give a conversion of 88.8% and an equilibrium constant of 63.0.

TABLE I

ESTERIFICATION EXPERIMENTS

Ratio of ethyl alcohol to acetic acid = 1:1. Temperature, 250°

Cc. of liquid per hour per 100 cc. of catalyst	109.0	46.2	25.0	13 4	13.0	10.0	5.6	4.2
Conversion to ester, %	24.8	44.8	58.5	72.2	74.0	78.8	82.8	85.0

Temperature, 280°

Cc. of liquid per hour per 100 cc. of catalyst	145.0	54.5	23.1	11.4	8.8	8.0	8.0	7.0	7.0	6.8
Conversion to ester, %	46.9	66.8	79.8	84.2	87.6	87.5	86.3	88.2	88.2	87.3

Temperature, 300°

Cc. of liquid per hour per 100 cc. of catalyst	150.0	15.4	14.6	13.6	13.5	12.0	11.1	10.4	8.4	5.0
Conversion to ester, %	47.0	87.2	85.6	85.0	84.5	88.7	87.2	88.9	89.7	89.8

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[5] Drucker and Ullmann, *Z. physik. Chem.*, 74, 567 (1910).

Experiments made with higher ratios of alcohol to acid gave correspondingly higher values for the percentage of acetic acid converted into ester. However, the results were not accurate enough to serve as a check of the equilibrium determinations since a relatively large error was introduced in analyzing for the small amount of unconverted acid in the condensate. With a 2:1 ratio of alcohol to acid, 98% of the acetic acid should be converted into ester at 280°, and in a qualitative way this was shown to be the case.

Above 300° side reactions began to become noticeable, as evidenced by olefin formation, presumably due to dehydration of the alcohol. Even at 325° the amount of olefin formed was sufficient to disturb the equilibrium determination. Without a catalyst there was no appreciable ester formation at the times of contact employed.

Table II gives the results of a series of hydrolysis experiments made at 280°. Since the ester and water were immiscible in the proportions used and, therefore, had to be introduced in separate streams, it was not possible to duplicate the ratio of the two from run to run. However, the feed rates and, consequently, the molal ratio of ester to water remained constant throughout individual experiments. From the composition of the condensate the equilibrium constant of the esterification reaction was calculated, as shown in the last column of Table II. The average value of the six determinations is 49.0, or exactly the same as that resulting from the esterification experiments. However, in view of the short time of contact employed, the first value cannot be considered representative of equilibrium conditions. By discarding this and the third value, which is out of line with the others and obviously too low, the average becomes 49.3. Even on this basis the agreement with the esterification value of 49.0 is better than the accuracy of the method warrants. Allowing for the errors in analysis and in material balance, the value of the equilibrium constant at 280° may be taken as 49 ± 4.

TABLE II

HYDROLYSIS EXPERIMENTS

Temperature, 280°

Cc. of liquid per hour per 100 cc. of catalyst	Moles in product				
	Ethyl acetate	Water	Acetic acid and ethyl alcohol	K	$1/K$
53.8	0.1125	0.1833	0.0192	0 0179	56.0
34.8	.0716	.0722	.0103	.0205	48.8
27.6	.0522	.0722	.0096	.0244	41.0
25.2	.0522	.0555	.0077	.0205	48.8
19.8	.0379	.0565	.0066	.0204	49.0
11.5	.0502	.0389	.0062	.0197	50.7

In Table III the results obtained in these experiments are compared with those available in the literature. The low figures reported by Mailhe and de Godon are not included, however, since it is apparent that the time of contact was too short for equilibrium to be reached in their experiments. With the exception of Edgar and Schuyler's results, the data in Table III show that the equilibrium concentration of ester is practically constant over a temperature range of 75 to 300°, although the relatively small differences in the conversion figures are magnified in the values for the equilibrium constant. The free energy change accompanying the reaction is not known with sufficient accuracy to permit calculation of the equilibrium constant. In a qualitative way, however, free energy computations give support to the small temperature coefficient indicated by the experiments. Of the writers' constants, the one for 280" is most dependable, considering that it has been determined by approaching the equilibrium from both directions.

Table III

Comparison of Equilibrium Data

Reaction: $C_2H_5OH + CH_3COOH = CH_3COOC_2H_5 + H_2O$

Basis: Equimolar mixtures of ethyl alcohol and acetic acid

	Temp.. °C.	Conversion to ester, %	Equilibrium constant
Edgar and Schuyler	72.6–77.6	About 95	347–559
Swietoslawski and Poznanski	75–76	88.5	59
Mulliken, Chappell and Reid	150	89.9	79.3
Frolich, Carpenter and Knox	280	87.5	49
Frolich, Carpenter and Knox	300	88.8	63

Summary

1. The vapor phase esterification of ethyl alcohol by acetic acid in the presence of a zirconium oxide catalyst has been studied over a temperature range of 250 to 300°.

2. At 250° the reaction proceeded too slowly for equilibrium to be reached in the flow system employed. Above 300° there was a tendency for simultaneous dehydration of the alcohol into ethylene. In the absence of catalyst no appreciable amount of ester was formed.

3. Esterification experiments with equimolar concentrations of ethyl alcohol and acetic acid gave 87.5% of ethyl acetate at 280°, corresponding to an equilibrium constant of 49.0. Hydrolysis of the ester by the reverse reaction gave a value of 49.3. In consideration of the possible error the value of the equilibrium constant at this temperature may be taken as 49 ± 4.

4. At 300° 88.8% conversion was obtained in esterification experiments but was not checked by the reverse reaction. This corresponds to an equilibrium constant of 63.

5. Comparison of these results with others reported in the literature shows that the equilibrium constant changes only slightly with temperature. It may therefore be concluded that the maximum conversion to

ester obtainable in this temperature range from equimolar concentrations of alcohol and acid is about 88 to 90%.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

THE IODINATION OF PHENOL AND CRESOL ETHERS

BY F. B. DAINS, A. W. MAGERS AND WALDO L. STEINER

RECEIVED OCTOBER 31, 1929 PUBLISHED APRIL 7, 1930

The introduction of iodine into aromatic hydrocarbons such as benzene, toluene, cymene, etc., using nitric acid as an oxidizing agent was first described by La Datta and Chatterjee.[1] The method has been studied in detail in this Laboratory and the following paper is an account of the reaction as applied to the phenol ethers. The free phenols are too reactive and the resulting products consist of nitro rather than the desired iodo compounds. When the phenol ethers are used, the reaction proceeds smoothly and in good yields. The interesting fact was also noted that iodine can be introduced into the nitro-anisoles and nitrophenetoles, although nitrobenzene is unaffected under the same conditions. A description of the general procedure is given in one instance; the other results are tabulated.

Experimental

I. Iodination of Phenetole.—Phenetole (20 g.) and iodine[2] (15 g.) were placed in a small Kjeldahl flask fitted with a ground in glass condenser and heated in an oil-bath at 180°. For higher temperatures a metal-bath can be used. From time to time 2–3-cc. portions of concentrated nitric acid were added through the condenser. After an hour's heating the iodine had practically disappeared. The residue in the flask was washed with alkali and steam distilled. In the iodination of cresol derivatives the alkali dissolves any substituted benzoic acids formed by oxidation. The oil was separated, dried and fractionated at 11 mm. It came over between 120 and 138° and on cooling part of it solidified. This when freed from oil melted at 28° and proved to be *p*-iodophenetole. The major portion of the oil (b. p. 240° at 730 mm.) corresponded in properties to the known o-iodophenetole. Additional evidence of its formation was given by the fact that in one run the main product was 2-iodo-4-nitrophenetole (m. p. 96°).[3]

V. 2-Nitro-4-iodo-anisole (m. p. 98°).—Reverdin[4] described this ether as melting at 73° but the following proof of structure would seem to confirm the higher melting point.

The nitration of *p*-acetanisidine and subsequent hydrolysis gave the 2-nitro-4-

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[1] Datta and Chatterjee, THIS JOURNAL, 39, 435 (1917).

[2] The addition of 3–5 cc. of pyridine increases the yield and lowers the temperature at which the reaction occurs.

[3] Reverdin, *Ber.*, 29, 2596 (1896).

[4] Reverdin, *ibid.*, 29, 1003, 2595 (1896); Bull. *soc. chim.*, [3] 15, 639 (1896); Brenans, *Compt. rend.*, 134, 360 (1902).

amino-anisole (m. p. 51°),[11] from which was obtained the above 4-iodo compound (m. p. 96°), confirmed by mixed melting point.

Anal. Calcd. for $C_7H_6INO_3$: N, 5.01. Found: N, 4.95, 5.04.

TABLE I

REAGENTS AND PRODUCTS

No.	Subs. iodinated and temperature, °C.	Product (yield)
II	o-Cresol methyl ether (140°)	1-Methoxy-2-methyl-4-iodobenzene (85%)[a]
III	m-Cresol methyl ether (165°)	1-Methoxy-3-methyl-4-iodobenzene[b]
IV	o-Cresol methyl ether (180")	1-Methoxy-2-iodo-4-methylbenzene[c] (80%)[7]
V	o-Nitro-anisole (160–180°)	2-Nitro-4-iodo-anisole
VI	p-Nitro-anisole (160–170")	2-Iodo-4-nitro-anisole[d]
VII	m-Nitro-anisole (160–170°)	3-Nitro-4-iodo-anisole[9,e]
VIII	m-Amino-anisole[f]	1-Methoxy-3-amino-6-iodobenzene[g](oil)

[a] Non-volatile with steam. Identical with the ether formed by the methylation of the phenol (m. p. 65°) obtained from 2-amino-5-iodobenzene.[5] [b] Constitution proved by synthesis from 1-methoxy-3-methyl-4-aminobenzene.[6] A little liquid 6-iodo derivative is also formed, as well as some methoxybenzoic acid. [c] Willgerodt isolated the 2- and 3-iodo isomers from the cresol ether and iodine chloride. We found no evidence of the 3-iodo isomer' (m. p. 75°). [d] When reduced it gave an amine (m. p. 74") whose hydrochloride melted at 170". Calcd.: N, 4.92. Found: N, 4.88. The results agree with the work of Brenans and Reverdin.[8] [e] 3-Nitro-4-iodophenetole was obtained from m-nitrophenetole. [f] Heated with iodine, calcium carbonate and water. [g] 2-Iodo-5-nitro-anisole (m. p. 127–128°)[10] on reduction gave an oil whose hydrochloride was identical with the preceding; analysis and mixed m. p.

CONSTANTS AND ANALYTICAL DATA

No.	M. p., °C.	Formula	Analyses, % Calcd.		Found	
II	74	C_8H_9IO	I	51.21	51.2	
III	75	C_8H_9IO	I	51.21	51.10	51.15
IV	(Oil, b. p. 240°)	C_8H_9IO	I	51.21	51.13	
V	98	$C_7H_8INO_2$	N	5.01	5.03	5.09
VI	96	$C_7H_8INO_2$		...	...	
VII	62	$C_7H_8INO_2$	N	5.01	4.98	
VIII	155–156	$C_7H_8INO\cdot HCl$	HCl	12.78	12.22	

When the 2-nitro-4-iodo-anisole was reduced, the amine and its acetyl derivative were identical with the compounds synthesized from *p*-acetanisidine.

1-Methoxy-2-nitrodiphenylurea from phenylisocyanate and the 2-nitro-4-amino-anisole melts at 164°.

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[5] Wheeler and Liddle, Am. Chem. J., 42, 501 (1909).

[6] Stadel, Ann., 217, 51 (1883); 259, 210 (1890); Khotinsky and Jacopson-Jacopmann, Ber., 42, 3097 (1909); Gibson, J. Chem. *Soc.*, 123, 1269 (1923).

[7] Willgerodt and Kornblum, J. prakt. Chem., [2] 39, 296 (1889); Schall and Dralle, Ber., 17, 2533 (1896).

[8] Brenans, *Compt.* rend., 134, 360 (1902); Reverdin, Ber., 29, 998 (1896); Bull. *soc. chim.*, [3] 15, 639 (1896).

[9] Reverdin, Ber., 29, 2597 (1896); *Bull. soc. chim.*, [3] 17, 115 (1898); Hahle, J. prakt. Chem., [2] 42, 74 (1891).

[10] Mendola and Eyre, Chem. *Zentr.*, II, 97 (1901).

[11] German patent 101,778; Reverdin and Bucky, Ber., 39, 2698 (1896).

Anal. Calcd. for $C_{14}H_{13}N_3O_4$: N, 14.63. Found: N, 14.41, 14.70.

VI. The 2-iodo-4-amino-anisole (m. p. 74°) can be easily made directly from *p*-anisidine by heating with calcium carbonate, iodine, water and ether. It must be extracted from the reaction product as it is not volatile with steam. Under like conditions #-phenetidine gives the 2-iodo-4-aminophenetole.[12]

The constitution of the 2-iodo-4-nitro-anisole was further proved by diazotizing 4-nitro-o-anisidine. The iodine compound melted at 96° and the identity was confirmed by analysis and mixed melting point.

1-Methoxy-4-nitro-2-diphenyl-urea from the nitro-anisidine and phenyl isocyanate melted at 192°.

Anal. Calcd. for $C_{14}H_{13}N_3O_4$: N, 14.63. Found: N, 14.70.

Summary

It has been shown that the methyl cresol ethers and the nitro-anisoles can be iodinated directly at temperatures of 160–180°, using nitric acid as an oxidizing agent. The methoxy group has the main directing influence in the position of the iodine.

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OP KANSAS]

THE CONSTITUTION OF CERTAIN CHLORO-IODO AND BROMO-IODO ANILINES AND BENZENES

BY F. B. DAINS AND A. W. MAGERS

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In the course of the study of the effect of halogens on the aromatic amines, it became necessary to prepare certain iodine substitution products of the chloro and bromo substituted anilines. The method of Wheeler was employed, wherein iodine was allowed to react with the amine in the presence of calcium carbonate and water.[1]

In the paper in question[2] the final determination of structure of some of the derivatives was from necessity left unsettled and the present work fills in the lacunae with some additional data.

Experimental

4-Bromo-2,6-di-iodo-aniline.[3]—The iodination of 4-bromo-2-iodo-aniline gave a di-iodo compound (m. p. 148°). When this was diazotized in alcohol solution, the product was the known 1-bromo-3,5-di-iodobenzene (m. p. 140°).[4]

Anal. Calcd. for $C_6H_3BrI_2$: Br, 19.53; 1, 62.09. Found: Br, 19.35; I, 62.01.

1-Bromo-3,4,5-tri-iodobenzene was prepared from the bromo-di-iodo-aniline

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[12] Reverdin, *Ber.*, 29, 2596 (1896).

[1] Wheeler and others, *Am. Chem. J.*, 42,441,448 (1909); 44, 127, 500 (1910).

[2] Dains, Vaughan and Janney, THIS JOURNAL, 40,931–936 (1918).

[3] Ref. 2, p. 932.

[4] Körner and Condardi, *Chem. Zentr.*, II, 1038 (1913); *Atti. Accad. Lincei.*, 22, 832 (1913).

(148°) by replacing the amino group by iodine. It is difficultly soluble in alcohol, non-volatile with steam and melts at 153°.

Anal. Calcd. for $C_6H_2BrI_3$: Br, 14.94; I, 71.21. Found: Br, 14.65; I, 70.91.

1-Amino-3-bromo-4-iodobenzene.[3]—The position of the iodine in the compound (m. p. 56°) formed by the iodination of m-bromo-aniline was determined as follows: on replacing the amino group by iodine, the bromo-di-p-iodobenzene (m. p. 68°) was formed. The same compound results when *p*-di-iodobenzene is heated with bromine and iron filings in carbon tetrachloride solution.

Anal. Calcd. for $C_6H_3BrI_2$: Br, 18.53; I, 62.09. Found: Br, 19.47; I, 61.96.

Constitution of the 1-Amino-4-chloro-2-iodobenzene[8] (m. p. 46") formed from iodine and p-chloro-aniline. Replacing the amino group by chlorine gave the known iodo-di-p-chlorobenzene (m. p. 21°), which is also formed when di-p-chlorobenzene is heated with iodine and nitric acid at 160°.

Structure of the *p*-Chloro-di-iodo-aniline[5] (m. p. 129°).—This is the final product when iodine reacts with either *p*-chloro-aniline or 4-chloro-2-iodo-aniline. Elimination of the amino group gave 1-chloro-3,5-di-iodobenzene[4] (m. p. 101°).

Anal. Calcd. for $C_6H_3ClI_2$: Cl, 9.72; I, 69.78. Found: Cl, 9.74; I, 69.86.

1-Chloro-3,4,5-tri-iodobenzene.—The chloro-di-iodo-aniline (m. p. 129°) was dissolved in concentrated sulfuric acid at 0° and treated with powdered sodium nitrate. Potassium iodide was added to the solution when the acid was poured on cracked ice. The white crystals from alcohol melted at 148°.

Anal. Calcd. for $C_6H_2ClI_3$: Cl, 7.23; I, 77.67. Found: Cl, 7.26; I, 78.00.

2-Amino-6-iodo-anisole.[6]—In the preceding paper, o-anisidine was found to yield with iodine a mono-iodo-o-anisidine (m. p. 49"). Position 6 of the iodine was determined by its transformation into 2,6-di-iodo-anisole (m. p. 35°) and into 4-nitro-2,6-di-iodo-anisole (m. p. 133–134°).[7]

Summary

The structures of some iodine derivatives of chloro- and bromo-aniline and of o-anisidine have been definitely determined.

LAWRENCE, KANSAS

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[5] Ref. 3, p. 933.

[6] Ref. 3, p. 935.

[7] Brenans, *Compt.* rend., 134,357 (1902); Bull. *soc. chim.*, [3] 27,401 (1902).

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

STUDIES OF CONJUGATED SYSTEMS. IV. THE ADDITION OF HYPOCHLOROUS AND HYPOBROMOUS ACIDS TO PHENYLBUTADIENE

BY IRVING E. MUSKAT AND LOREN B. GRIMSLEY

RECEIVED NOVEMBER 1, 1929 PUBLISHED APRIL 7, 1930

The addition reactions of conjugated systems have been for some time the subject of an investigation in this Laboratory. The problem has been attacked from several points of view: (1) to accumulate accurate data as to the type of addition, 1,2, 1,4 or 3,4, taking place in conjugated systems; (2) to study the influence of the directing group R, in $R—CH=CH—CH=CH_2$, on the type of addition; (3) to study the effect of different addenda on the type of addition, *i. e.*, to determine whether or not the type of addition was dependent on the nature of the addition reagent; (4) to attempt to correlate the data on conjugated systems and interpret them according to an electronic formulation of conjugated systems; and (5) to show the connection of conjugated systems to aromatic compounds. For our preliminary investigations we have chosen to study the addition reactions of phenylbutadiene ($C_6H_5CH=CHCH=CH_2$) and vinylacrylic acid ($HOOC-CH=CHCH=CH_2$), for these conjugated systems afforded us an opportunity to study the problems of immediate interest to us.

Thiele[1] proved that vinylacrylic acid was reduced in the 1,4-position and not in the 1,2-position as claimed by Doebner.[2] Muskat, Becker and Lowenstein[3] have studied the chlorination and bromination of vinylacrylic acid and found that both chlorine and bromine are absorbed in the 3,4-position. They also found that 3-chloro- and 3-bromo-vinylacrylic acids absorb chlorine and bromine, respectively, in the 3,4-position.

Klages[4] studied the reduction of phenylbutadiene and found that hydrogen is absorbed in the 1,4-position. On the other hand, Strauss[5] proved that phenylbutadiene added bromine in the 3,4-position and not in the 1,4-position as claimed by Riiber.[6] Muskat and Huggins[7] confirmed Strauss's work and also studied the chlorination of phenylbutadiene. They showed that both phenylbutadiene and 1-phenyl-4-chloro-butadiene add chlorine in the 3,4-position and not in the 1,4-position, as postulated

[1] Thiele, *Ber.*, **35, 2320 (1902).**

[2] Doebner, *ibid.*, **35, 1136 (1902).**

[3] Muskat, Becker and Lowenstein, THIS JOURNAL, **52, 326 (1930);** (b) **52, 812 (1930);** see also Farmer, *J. Chem. Soc.*, **130, 1060 (1927).**

[4] Klages, *Ber.*, **37, 2301 (1904).**

[5] Strauss, *ibid.*, **42, 2866 (1909).**

[6] Riiber, *ibid.*, **36, 1404 (1903).**

[7] Muskat and Huggins, THIS JOURNAL, **51,2496 (1929).**

by Thiele. In continuation of this work Huggins[8] has found that phenylbutadiene adds hydrogen chloride and hydrogen bromide exclusively in the 3,4-position. The present paper contains the results of an investigation on the addition of hypochlorous and hypobromous acids to phenylbutadiene.

A search of the literature revealed but one paper reporting a study of the addition of the hypohalous acids to conjugated systems. Mokiewsky[9] prepared the dichlorohydrin and dibromohydrin of isoprene but did not determine the structure of these compounds. He did not prepare the mono-addition derivatives, and to the best of our knowledge no such derivative of a conjugated compound has been reported. Przybytek studied the addition of hypochlorous acid to a number of diolefins but did not include in his investigation any member of a conjugated system.

The addition of hypochlorous acid to phenylbutadiene was first studied. It was found that phenylbutadiene readily absorbs one molecule of hypochlorous acid to form a monochlorohydrin. The structure of the monochlorohydrin was determined, in part, by ozonization. Six monochlorohydrins are theoretically possible, depending on whether 1,2-, 1,4- or 3,4-addition takes place and also on the orientation of the hypochlorous acid in the molecule of phenylbutadiene. On ozonizing the phenylbutadiene monochlorohydrin it was possible to obtain a 76% yield of benzaldehyde as calculated from its semicarbazone. No effort was made to identify the second oxidation product, the α-hydroxy-β-chloropropionic aldehyde or the α-chloro-β-hydroxypropionic aldehyde, since the instability of either proscribes its use for the determination of the structure of the chlorohydrin. This proves that hypochlorous acid adds to phenylbutadiene in the 3,4-position, with the formation of a chlorohydrin having the structure I or II.

I $C_6H_5CH{=}CH{-}CH(OH)CH_2(Cl)$ II $C_6H_5CH{=}CH{-}CH(Cl)CH_2(OH)$

In order to distinguish between these two possible structures, I and II, the decomposition products of the chlorohydrin were studied. It was observed that the monochlorohydrin, on distillation under reduced pressure, decomposes with the liberation of water and hydrogen chloride. One of the decomposition products was identified as 1-phenyl-4-chlorobutadiene, which was obviously formed by the elimination of water from the chlorohydrin. This proves that phenylbutadiene chlorohydrin has the structure I, $C_6H_5CH{=}CHCH(OH)CH_2Cl$. The residue from the distillation of the chlorohydrin yielded yellow crystals, m. p. 235°, which analyzed for $C_{10}H_{10}$, which is the empirical formula of phenylbutadiene. It is of interest as one of the few hydrocarbons possessing color.

Phenylbutadiene chlorohydrin readily absorbs two atoms of chlorine to give a trichloride whose structure, based on its method of preparation, is probably $C_6H_5CHClCHClCH(OH)CH_2Cl$.

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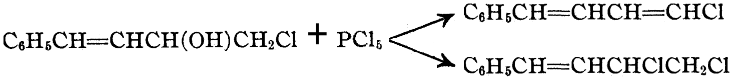
[8] To be published soon.

[9] Mokiewsky, *J. Russ. Phys.-Chem. Soc.*, 30, 885 (1898).

Phenylbutadiene chlorohydrin was treated with phosphorus pentachloride in dry ether. Two reaction products were isolated: a lower-boiling fraction which proved to be 1-phenyl-4-chlorobutadiene, and a higher-boiling compound which was identified as 3,4-dichlorophenylbutene. In the first reaction phosphorus pentachloride played the role of a dehydrating agent; in the second reaction, that of a chlorinating agent. These two concurrent reactions may be represented as follows

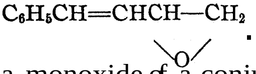


$$C_6H_5CH{=}CHCH(OH)CH_2Cl + PCl_5 \begin{cases} \nearrow C_6H_5CH{=}CHCH{=}CHCl \\ \searrow C_6H_5CH{=}CHCHClCH_2Cl \end{cases}$$

Phenylbutadiene chlorohydrin readily absorbs a molecule of hypochlorous acid to form a dichlorohydrin. Its structure was not determined but it probably consisted of a mixture of stereoisomers of 1-phenyl-1,3-dihydroxy-2,4-dichlorobutane, $C_6H_5CH(OH)CHClCH(OH)CH_2Cl$.

If phenylbutadiene chlorohydrin is treated with an excess of hypochlorous acid, trichlorohydroxyphenylbutane is formed. The first step in the reaction probably is the formation of the dichlorohydrin of phenylbutadiene, which then reacts with the excess of hypochlorous acid to give the trichloro derivative. We did not determine its structure, but from the fact that its boiling point, 164° under 5-mm. pressure, and general behavior were the same as the product obtained by the chlorination of phenylbutadiene chlorohydrin, its probable structure is $C_6H_5CHClCHClCH(OH)CH_2Cl$.

An effort was made to prepare the oxide of phenylbutadiene from its chlorohydrin by the usual methods. It was not possible to prepare a pure oxide since the chlorine was not completely removed.[10] The oxide distilled at about 94° under 6-mm. pressure and must have the structure,



$$C_6H_5CH{=}CH\underbrace{CH{-}CH_2}_{\diagdown O \diagup}$$

. To the best of our knowledge this is the first time a monoxide of a conjugated system has been reported.[11]

The addition of hypobromous acid to phenylbutadiene was then studied. It was found that phenylbutadiene readily absorbed one molecule of hypobromous acid to form a monobromohydrin. The structure of the monobromohydrin was determined in a manner entirely analogous to that used for the chlorohydrin. The isolation and identification of benzaldehyde as one of the oxidation products of the bromohydrin proved that it also was a 3,4-addition product of phenylbutadiene.

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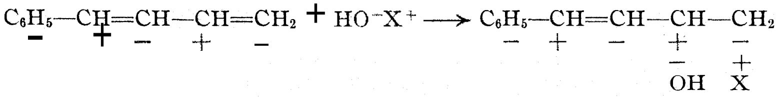
[10] This is in accord with previous reports on the preparation of oxides from the chlorohydrins. See Przybytek, *Ber.*, 17, 1090 (1884); 20, 3239 (1887). It is possible that the potassium hydroxide dehydrates the chlorohydrin to give 1-phenyl-4-chlorobutadiene, from which the chlorine can be removed only with great difficulty. A similar interpretation might hold for other chloro- and bromohydrins.

[11] A complete investigation of the oxidation of conjugated systems is now under way in this Laboratory. On oxidizing phenylbutadiene with perbenzoic acid a 1,2-monoxide is formed.

Phenylbutadiene bromohydrin readily absorbs a molecule of hypobromous acid to form a dibromohydrin. Its structure was not determined but it probably consisted of a mixture of stereoisomers of 1-phenyl-1,3-dihydroxy-2,4-dibromobutane, $C_6H_5CH(OH)CHBrCH(OH)CH_2Br$.

It was much easier to prepare the phenylbutadiene oxide from the monobromohydrin than from the chlorohydrin. The oxide prepared from the bromohydrin contained but a trace of bromine.

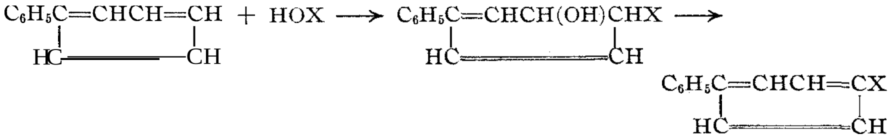
The orientation of the hypochlorous and hypobromous acids in the molecule of phenylbutadiene may be interpreted readily according to the electronic formulations developed by Muskat and Becker[3b]



$$\underset{-}{C_6H_5}-\underset{+}{CH}=\underset{-}{CH}-\underset{+}{CH}=\underset{-}{CH_2} + HO^-X^+ \longrightarrow \underset{-}{C_6H_5}-\underset{+}{CH}=\underset{-}{CH}-\underset{\substack{+\\-\\OH}}{CH}-\underset{\substack{-\\+\\X}}{CH_2}$$

This would also explain the ease of eliminating water from the chloro- and bromohydrins, as compared to the difficulty encountered in removing the halogen, X+. It would be expected from these considerations that the isomeric chloro- and bromohydrins, $C_6H_5CH=CHCH(X)CH_2(OH)$, should lose HX very easily to give a pure oxide. Further work in this direction is now under way.

The elimination of water from the chlorohydrin to give 1-phenyl-4-chlorobutadiene corresponds to the para-chlorination of diphenyl in the aromatic series and suggests that para-halogenation in the aromatic series is preceded by the 3,4-addition of X^-X^+ or HO^-X^+ rather than by 1,4-addition.



Experimental Part

Phenylbutadiene **Chlorohydrin.**—Phenylbutadiene was prepared according to the method of Muskat and Ludeman[12] by the condensation of cinnamic aldehyde with methylmagnesium bromide and the hydrolysis of the intermediate Grignard addition compound with 30% sulfuric acid. Hypochlorous acid was prepared according to the method of Reformatzky[13] by passing chlorine into a finely divided suspension of mercuric oxide in water at about −5°. A 3–5% solution of hypochlorous acid, free from chlorine, was used in these experiments.

Phenylbutadiene was treated with one mole of a dilute hypochlorous acid solution. The hypochlorous acid must be added slowly and under continuous agitation and cooling, otherwise the reaction becomes too violent. The rate of reaction can be followed readily by the usual iodimetric titrations. After all of the hypochlorous acid had been added, the reaction mixture was allowed to stand overnight. The reaction mixture was taken up in ether, washed free of chlorides, dried over sodium sulfate and the ether

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[12] Muskat and Ludeman, *Ber.*, 62, 2284 (1929).

[13] Reformatzky, *J. prakt. Chem.*, 40, 396 (1889).

was removed by suction at ordinary temperature. The chlorohydrin is unstable at higher temperatures and decomposed when distilled even at reduced pressure. It was analyzed for chlorine in the usual manner.

Anal. Calcd. for $C_{10}H_{11}OCl$: Cl, 19.43. Found: Cl, 19.35, 19.26.

The phenylbutadiene chlorohydrin (5 g.), dissolved in chloroform, was subjected to ozonization for several hours. The process of ozonization and the method of working up the oxidized fractions are amply described by Muskat and Huggins.[7] It was possible to recover 3.4 g. of the semicarbazone of benzaldehyde, which corresponds to a 76% yield of benzaldehyde. It was not possible to obtain the slightest indication of the presence of any of the aldehydes or acids to be expected from the oxidation of compounds formed by the 1,2- or 1,4-addition of hypochlorous acid to phenylbutadiene.

When phenylbutadiene chlorohydrin was distilled under reduced pressure, decomposition set in with the liberation of water and hydrogen chloride. A product distilled over at 104–120" under 13-mm. pressure which solidified when placed in a freezing mixture. The crystals were pressed out on a porous plate. They melted sharply at 52°, the melting point of 1-phenyl-4-chlorobutadiene. A mixture with a sample of known origin also melted at 52°. The residue, a black tarry mass, was extracted a number of times with hot benzene. The benzene solution was concentrated and cooled and yellow crystals separated; these were purified by a number of crystallizations from various solvents, but the yellow color remained. It is not very soluble in any solvent; it is more soluble in hot benzene and ether than in the other ordinary organic solvents. It melts at 235° and was analyzed by micro-methods.

Anal. Calcd. for $C_{10}H_{10}$: C, 92.25; H, 7.75. Found: C, 92.22; H, 7.73.

Reactions of Phenylbutadiene Chlorohydrin.—Phenylbutadiene chlorohydrin was chlorinated by allowing a stream of chlorine gas to pass into a solution of the chlorohydrin in chloroform. Absorption took place readily. When the theoretical quantity of chlorine was absorbed, the reaction mixture was distilled under reduced pressure. A light yellow oil distilled over at 164" under 5-mm. pressure. On standing it assumed a greenish color, and finally, after standing for several days, it turned to a dark green color.

Anal. Calcd. for $C_{10}H_{11}OCl_3$: Cl, 41.97. Found: Cl, 41.92, 41.97.

Phenylbutadiene chlorohydrin was treated with phosphorus pentachloride in dry ether. The reaction mixture was allowed to stand overnight. It was then taken up in ether, washed free of chlorides, dried and the ether was removed by vaporization. The residual oil was distilled under reduced pressure. Two fractions were collected: one distilling at 140–150° under 16-mm. pressure, the second distilling at 150–160° under 16-mm. pressure. The first fraction was redistilled, the major portion coming over at 115–117° under 3.5-mm. pressure, the boiling point of 1-phenyl-4-chloro-butadiene. It solidified when placed in a freezing mixture. The crystals melted at 50° and did not lower the melting point of known 1-phenyl-4-chlorobutadiene when mixed with it. The second fraction was also redistilled, the main portion coming over at 140" under 10-mm. pressure, the boiling point of 3,4-dichloro-1-phenylbutadiene. A chlorine analysis verified this conclusion.

Phenylbutadiene chlorohydrin was treated with one mole of hypochlorous acid solution. Absorption took place fairly readily with the formation of a viscous oil. The oil could not be crystallized even when placed in a carbon dioxide snow and ether mixture. It is unstable toward distillation even under reduced pressure. It is obviously a dichlorohydrin of phenylbutadiene.

Anal. Calcd. for $C_{10}H_{12}O_2Cl_2$: Cl, 30.18. Found: Cl, 30.22, 30.18.

Phenylbutadiene chlorohydrin was treated with a large excess of hypochlorous acid and the reaction mixture was allowed to stand overnight. The oily layer was taken up in ether, washed free from chlorides, dried and the ether was removed by vaporization. The residual oil was distilled under reduced pressure. A light yellow oil distilled over at 164–167° under 5-mm. pressure. On standing it assumed a greenish color, which finally, after standing for several days, turned to a dark green.

Anal. Calcd. for $C_{10}H_{11}OCl_3$: Cl, 41.97. Found: Cl, 41.93.

A number of attempts were made to prepare the oxide of phenylbutadiene from its chlorohydrin. Finely divided potassium acetate, silver nitrate, alkali in alcohol and acetone solution and finely powdered potassium hydroxide were used under widely different experimental conditions in an effort to prepare the pure oxide. Of all the methods tried, the one using powdered potassium hydroxide in dry ether was found, on the whole, to be most satisfactory. However, a pure oxide could not be prepared even by this method. It was not possible to remove completely all of the chlorine. The impure oxide obtained by this method distilled at 94° under 6-mm. pressure.

Phenylbutadiene Bromohydrin.—Phenylbutadiene was treated with the theoretical quantity of a dilute hypobromous acid solution. Its method of preparation is identical with that described for the preparation of the chlorohydrin. The bromohydrin is far less stable than the corresponding chlorohydrin. It was stable only when dissolved in an organic solvent. Working very rapidly, it was once possible to obtain a sample for analysis.

Anal. Calcd. for $C_{10}H_{11}OBr$: Br, 35.20. Found: Br, 35.34.

The phenylbutadiene bromohydrin (4.6 g.), dissolved in chloroform, was subjected to ozonization and the ozonide thus formed was worked up in a manner entirely analogous to that described for the chlorohydrin. It was possible to recover 2.6 g. of the semicarbazone of benzaldehyde which was identified by its melting point and a melting point of a mixture with a sample of known origin. This corresponds to a 78% yield of benzaldehyde: It was not possible to obtain even the slightest indication of the presence of any of the aldehydes or acids to be expected from the oxidation of compounds formed by the 1,2- or 1,4-addition of hypobromous acid.

Reactions of Phenylbutadiene Bromohydrin.—Phenylbutadiene bromohydrin was treated with one mole of a dilute hypobromous acid solution. Absorption took place fairly rapidly with the formation of a very viscous oil, which could not be crystallized. It is unstable toward distillation even under reduced pressure. It is obviously a dibromohydrin of phenylbutadiene.

Anal. Calcd. for $C_{10}H_{12}O_2Br_2$: Br, 49.34. Found: Br, 49.30, 48.83.

On treating an ethereal solution of phenylbutadiene bromohydrin with powdered potassium hydroxide, the 3,4-monoxide of phenylbutadiene was formed. The oxide prepared from the bromohydrin was purer than that prepared from the chlorohydrin.

Summary

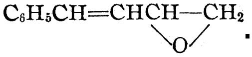
1. Phenylbutadiene absorbs hypochlorous and hypobromous acid in the 3,4-positions to form 3-hydroxy-4-chloro-1-phenylbutadiene and 3-hydroxy-4-bromo-1-phenylbutadiene, respectively.

2. Phenylbutadiene chlorohydrin decomposes, on distillation, to give 1-phenyl-4-chlorobutadiene and *a* residue from which was extracted *a* yellow hydrocarbon, which is ***a*** polymer of phenylbutadiene.

3. Phenylbutadiene chlorohydrin reacts with phosphorus pentachloride to give, by dehydration, 1-phenyl-4-chlorobutadiene, and, by chlorination, 3,4-dichlorophenylbutene.

4. Phenylbutadiene chlorohydrin readily absorbs a molecule of chlorine to give 1-phenyl-1,2,4-trichloro-3-hydroxybutane.

5. Phenylbutadiene chlorohydrin absorbs a molecule of hypochlorous acid to give a dichlorohydrin. In the same way phenylbutadiene bromohydrin absorbs a molecule of hypobromous acid to give a dibromohydrin

6. On treating with powdered potassium hydroxide, both phenylbutadiene chlorohydrin and bromohydrin lose a molecule of hydrogen chloride and hydrogen bromide, respectively, to give a monoxide of phenylbutadiene,  $C_6H_5CH{=}CHCH{-}CH_2$ (—O—). This is the first time a monoxide of a conjugated compound has been reported.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON PYRIMIDINES. CXIV. THE REARRANGEMENT OF 2-ETHYLMERCAPTO-5-CARBETHOXY-6-THIOCYANPYRIMIDINE INTO ITS ISOTHIOCYANATE MODIFICATION[1]

BY TREAT B. JOHNSON AND YUOH FONG CHI

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The behavior of several chloropyrimidines toward potassium thiocyanate has been described in previous papers from this Laboratory,[2] but of all the different pyrimidine halides thus far studied in our thiocyanate researches no one has proved to be more interesting than 2-ethylmercapto-5-carbethoxy-6-chloropyrimidine, II, which was first described by Wheeler and Johns.[3] They prepared it by the action of phosphorus oxychloride on 2-ethylmercapto-5-carbethoxy-6-oxypyrimidine, I.

$$NHC(SC_2H_5){=}NCH{=}C(COOC_2H_5)CO$$

I

$$NC(SC_2H_5){=}NCH{=}C(COOC_2H_5)CCl$$

II

$$NC(SC_2H_5){=}NCH{=}C(COOC_2H_5)CSCN$$

III

$$NC(SC_2H_5){=}NCH{=}C(COOC_2H_5)CNCS$$

IV

$$NC(SC_2H_5){=}NCH{=}C(COOC_2H_5)CNH_2$$

V

2-Ethylmercapto-5-carbethoxy-6-chloropyrimidine, II, is another example of a halide in the pyrimidine series which interacts in a characteristic manner with potassium thiocyanate, giving a normal thiocyanate deriva-

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[1] Constructed from part of a dissertation presented by Yuoh Fong Chi to the Faculty of the Graduate School of Yale University in June, 1928, in partial fulfilment of the requirements for the Ph.D. degree.

[2] Wheeler and Bristol, THIS JOURNAL, 23, 287 (1901); Johnson and McCollum, *Am. Chem. J.*, 36, 136 (1906); Johnson and Storey, *ibid.*, 40, 138 (1908).

[3] Wheeler and Johns, *Am. Chem. J.*, **38**, 594 (1907).

tive, III. The rhodanide which is formed represents, however, a more stable structure than that revealed by any of the combinations previously studied. While the thiocyanate III can be distilled without decomposition, and without conversion to its isomeric isothiocyanate form, IV, its stability is influenced by the presence of certain reagents and a molecular rearrangement to the isothiocyanate can be accomplished at temperatures much below that of its boiling point. The conditions under which this change is brought about are discussed in the experimental part of this paper.

It has previously been shown in our paper on pyrimidine thiocyanates that chloropyrimidines corresponding in structure to II interact with potassium thiocyanate in absolute alcohol to give their corresponding pyrimidine thionurethans. In such reactions the first product of change is the thiocyanate, which then undergoes rearrangement to give the isothiocyanate modification. This latter compound, however, has a momentary existence only under the conditions of reaction and interacts immediately with the alcohol, when formed, to give the corresponding thionurethan derivative.

The thiocyanate III does not undergo a rearrangement to IV at the temperature of boiling alcohol. When heated with alcohol at 150°, however, the normal conversion is brought about, but the yield of thionurethan obtained under such conditions is only about 40% of the theoretical. We now find that this low yield of thionurethan can be accounted for by the formation of 2-ethylmercapto-5-carbethoxy-6-aminopyrimdne V. Not only does this latter compound account for the remainder of the reaction products, but we also have been able to show that, if the heating with alcohol is continued for a prolonged period (six hours) the thiocyanate is transformed almost completely into the corresponding amino compound. In other words, the thionurethan is destroyed by the prolonged action of alcohol. This is the first case so far observed in which we have been able to obtain directly from a thiocyanate an aminopyrimidine in good yield by interaction with alcohol. The mechanism of the change may be explained in the following manner: by interaction of the pyrimidine chloride II with potassium thiocyanate in alcohol solution, the rhodanide III is first formed, and is rearranged to the isothiocyanate or mustard oil, IV. This in turn then combines with a molecule of ethyl alcohol, giving a thionurethan, which under the conditions of the experiment reacts with alcohol to form the aminopyrimidine, V.

This interesting behavior of absolute alcohol toward the pyrimidine thiocyanate III opens up a new method of preparing amino compounds in the pyrimidine series by direct replacement of an SCN radical by NH_2 without the use of ammonia. A corresponding change was observed early in our researches on pyrimidines by Wheeler and Bristol,[4] who obtained 2-ethylmercapto-5-bromo-6-thiopyrimidine and the corresponding 6-aminopy-

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[4] Wheeler and Bristol, *Am. Chem. J.*, 33, 452 (1905).

rimidine in small amount by digesting 2-ethylmercapto-5-bromo-6-chloropyrimidine in alcohol solution with potassium thiocyanate. This reaction will probably prove of value for synthesis in cases where it is impossible to introduce an amino group in place of a halogen by heating with ammonia, without replacing other radicals or groupings at the same time.

Experimental Part

2-Ethylmercapto-5-carbethoxy-6-chloropyrimidine, 11.—This pyrimidine was prepared according to the directions of Wheeler and Johns.[3] The yield from 13 g. of the mercapto-oxypyrimidine was 10 g. of the chloride boiling at 203° under a pressure of 20 mm.

2-Ethylmercapto-5-carbethoxy-6-thiocyanpyrimidine, 111.—This thiocyanate can be obtained by the action of potassium thiocyanate on the above chloride in boiling alcohol, benzene, xylene, toluene or acetone solutions. Ten grams of the chloropyrimidine, boiling at 203° at 20 mm. pressure, and 4 g. of potassium thiocyanate are dissolved in 200 cc. of 95% alcohol and the solution refluxed on a steam-bath for one hour, when the reaction is complete. The solution is then filtered while hot and chilled, when the thiocyanate separates immediately in the form of colorless plates. The yield was 9 g. or 82% of the theoretical. After purification by crystallization from alcohol, it melted at 104–105° to a colorless oil and distilled at 204–205° under a pressure of 4 mm. The thiocyanate is insoluble in alkali, but soluble in benzene, toluene and xylene. very soluble in hot alcohol, and insoluble in petroleum ether.

Anal. Calcd. for $C_{10}H_{11}O_2N_3S_2$: N, 15.61. Found: N, 15.90, 15.60, 15.91.

The alcohol filtrate remaining after the separation of the above thiocyanate was evaporated to complete dryness and the residue obtained then triturated with cold dilute sodium solution. On acidifying this alkaline solution with acetic acid, 0.6 g. of a yellow compound separated in crystalline condition. After recrystallization from 95% alcohol, this melted at 180–181° with decomposition. The analytical values for nitrogen indicated that we are dealing here with 2-ethylmercapto-6-thionethylurethan-pyrimidine-5-carboxylic acid, $\overline{\mathrm{NC(SC_2H_5){=}NCH{=}C(COOH)C}}\mathrm{NHCSOC_2H_5}$ (see below).

Anal. Calcd. for $C_{10}H_{13}O_3N_3S_2$: N, 14.63. Found: N, 14.38.

Proof of Structure of the **Thiocyanate.**—That the compound described above (melting at 104–105°) is to be represented by a normal rhodanide or thiocyanate structure is established by the following experimental facts: (1) it does not undergo any change leading to formation of a thiourea when exposed to the action of concentrated aqueous ammonia; (2) it can be crystallized from hot alcohol without conversion to a thiourethan, and (3) the compound interacts with thioacetic acid[6] to form the dithiourethan described below.

2-Ethylmercapto-5-carbethoxypyrimidine-6-acetyldithiourethan, $\overline{\mathrm{NC(SC_2H_5){=}NCH{=}C(COOC_2H_5)C}}\mathrm{SCSNHCOCH_3}$.—Two grams of 2-ethylmercapto-5-carbethoxy-6-thiocyanopyrimidine was dissolved in 10 cc. of thioacetic acid and the solution warmed on a steam-bath for eight to ten hours. The solution was then evaporated to dryness to remove the excess of the thio-acid and the sirupy residue brought to crystallization by trituration with alcohol. This product was purified by crystallization from boiling 95% alcohol and it separated on cooling in the form of yellow plates melting at 142–143°.

Anal. Calcd. for $C_{12}H_{15}O_3N_3S_3$: N, 12.17. Found: N. 12.20.

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[5] Wheeler and Merriam, This Journal, 23, 283 (1901).

The compound exhibited all the properties of a dithiourethan. It dissolved in cold alkali solution and was reprecipitated unaltered from such solutions by addition of acetic acid.

The Molecular Rearrangement of 2-Ethylmercapto-5-carbethoxy-6-thiocyanpyrimidine into its Isomeric Form, IV

2-Ethylmercapto-5-carbethoxy-6-isothiocyapyrde IV.—The best procedure for preparing this mustard oil is as follows. Five grams of the above thiocyanate is dissolved in 50 cc. of benzene and the solution heated at 190° for seven and one-half hours. When the tube was examined the solution was colored dark red. After evaporating the benzene, in which the isothiocyanate is very soluble, the latter was then extracted with petroleum ether, the solution concentrated and finally chilled, when the isothiocyanate separated in the form of prisms melting at 32–33° to an oil. The yield obtained was about 75%.

Anal. Calcd. for $C_{10}H_{11}O_2N_3S_2$: N, 15.61. Found: N, 15.68, 15.62.

Proof of Structure of the Isothiocyanate, IV. Reactivity toward Amines with Formation of Thioureas

2-Ethylmercapto-5-carbethoxy-6-thiourea-pyrimidine.—Two grams of the thiocyanate III was rearranged to the isothiocyanate IV as described above and the latter then separated in petroleum ether solution. On passing dry ammonia gas into this solution two grams of the above thiourea precipitated in crystalline form. After purifying by crystallization from ether, it melted at 165–168°.

Anal. Calcd. for $C_{10}H_{14}O_2S_2N_4$: N, 19.58. Found: N, 19.72, 19.60.

2-Ethylmercapto-5-carbethoxy-6-phenylthiourea-pyrimidine.—This is formed in quantitative yield by the action of aniline on the isothiocyanate in cold petroleum ether solution. It crystallizes from 95% alcohol in prisms which melt at 134–135° to an oil.

Anal. Calcd. for $C_{16}H_{18}O_2S_2N_4$: N, 15.47. Found: N, 15.36, 15.40.

2-Ethylmercapto-6-thionethylurethan-pyrimidine-5-carboxylic Acid.—One gram of the thiocyanate was rearranged to the isothiocyanate modification, then dissolved in 10 cc. of absolute alcohol and the solution boiled for one hour. On cooling, the urethan separated. This was then dissolved in dilute sodium hydroxide solution to saponify the ester grouping, and the alkaline solution then acidified with acetic acid, when 0.7 g. of the above thionurethan-carboxylic acid separated. After crystallization from alcohol it melted at 180–181°.

Anal. Calcd. for $C_{10}H_{13}O_3N_3S_2$: N, 14.63. Found: N, 14.45, 14.55.

Conditions Affecting the Rearrangement of the Thiocyanate, 111.—While the thiocyanate can be distilled under diminished pressure without change into its isothiocyanate modification, IV, it can be rearranged at a temperature much lower than its boiling point. Rearrangement can be brought about by prolonged heating at 160–170°, but below this temperature the change is very slow. At 180–190° rapid change takes place, but the rearrangement is accompanied by secondary changes which lead to a reaction product which is very hard to purify. Dry heating is not recommended for accomplishing the thiocyanate rearrangement. Heating in benzene solution at 150° for six hours produced no change. At 160° partial rearrangement had taken place after heating for seven hours, and from the solution both the thiocyanate and isothiocyanate were separated, melting at 32–33 and 104°, respectively. Heating at 190° in either toluene or benzene solution leads to a complete molecular rearrangement. A specimen of the thiocyanate III which had been preserved in a bottle for over two years was found to have suffered no change and melted at 104–105°.

Rearrangement by Heating in Alcohol.—At the boiling point of ethyl alcohol the thiocyanate III undergoes no rearrangement and can be recrystallized repeatedly from this solvent without alteration. On the other hand, when heated in alcohol at 150° (54° below its boiling point) the rhodanide is transformed completely into its isothiocyanate form, IV. This is formed as an intermediate product of reaction which then combines with the solvent, giving 2-ethylmercapto-5-carbethoxy-6-thionurethan-pyrimidine, $\overline{\mathrm{NC(SC_2H_5)=NCH=C(COOC_2H_5)C}}\mathrm{NHCSOC_2H_5}$.

Ten grams of the thiocyanate III dissolved in 100 cc. of absolute alcohol was heated at 150° for two hours. When the tube was opened, 5 g. of a crystalline compound had separated. This crystallized from boiling alcohol in the form of prisms and melted at 119° to an oil. It gave the analytical results recorded below when analyzed for nitrogen and sulfur, indicating that the above thionurethan was the compound with which we were dealing.

Anal. Calcd. for $C_{12}H_{17}O_3N_3S_2$: N, 13.33; S, 20.34. Found: N, 13.23. 13.11. 13.22; S, 19.95, 20.18.

The alcohol filtrate from filtration of the above thionurethan was evaporated to dryness and the residue obtained triturated with dilute hydrochloric acid. Neutralization of the acid solution with ammonia produced an immediate crystalline precipitate weighing 3.5 g. which crystallized from dilute alcohol (50%) in plates melting at 101–102". The compound gave no test for sulfur and it was identified as 2-ethylmercapto-5-carbethoxy-6-aminopyrimidine, $\overline{\mathrm{NC(C_2H_5)=NCH=C(COOC_2H_5)C}}\mathrm{NH_2}$.

Conversion to this aminopyrimidine to the extent of 90% of the theoretical was accomplished by heating 10 g. of the thiocyanate III in alcohol at 150° for six hours. It crystallized in rectangular plates melting at 101–102° and when mixed with the aminopyrimidine prepared according to the method of Wheeler and Johns,[3] the melting point was not altered. A mixture of this pyrimidine and the thiocyanate III melted at 78". This pyrimidine is moderately soluble in cold alcohol, and insoluble in water.

Anal. Calcd. for $C_9H_{13}O_2N_3S$: N, 18 50; S, 14.11. Found: N, 18.40, 18.47; S, 14.40, 14.42, 14.05.

Summary

1. 2-Ethylmercapto-5-carbethoxy-6-chloropyrimidine interacts normally with potassium thiocyanate to form a true thiocyanate derivative, 2-methylmercapto-5-carbethoxy-6-thiocyanpyrimidine.

2. This thiocyanate can be rearranged smoothly under certain experimental conditions into its isomeric isothiocyanate. Both the thiocyanate and isothiocyanate can be obtained as crystalline compounds.

3. The 2-ethylmercapto-5-carbethoxy-6-isothiocyanopyrimidine interacts with ethyl alcohol, at its boiling point, to form the corresponding thiourethan derivative. If the latter is heated, however, with alcohol at 150° for several hours, there is formed in almost quantitative yield 2-ethylmercapto-5-carbethoxy-6-aminopyrimidine. This is a new method for converting pyrimidine thiocyanates into their corresponding aminopyrimidines, or for replacing a —SCN group by $—NH_2$.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

SYNTHESIS OF THIAZOLES CONTAINING PHENOL AND CATECHOL GROUPS. II

BY C. M. SUTER[1] AND TREAT B. JOHNSON

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Several thiazoles containing the catechol grouping have been described in a recent paper from this Laboratory by Johnson and Gatewood.[2] In all of these combinations the catechol nucleus occupied Position 4 of the thiazole cycle. This series of thiazole-phenol combinations has now been increased by the synthesis of the twelve new derivatives recorded in Table I of this paper. The object has been to obtain for pharmacological study a series of aromatic derivatives containing the phenolic nucleus in both positions, 2 and 4, of the thiazole ring. Especially interesting are the different catechol combinations, which are characterized by their remarkable stability.

The halogenated ketones which have been employed in this research have been chloro-acetocatechol, bromo-acetal and chloro-acetone. By interaction of these halides with the required thioamide combinations all the thiazoles recorded have been synthesized by a general method of preparation. Every one of these new thiazoles has proved to be a crystalline substance of marked stability, and all are sufficiently basic to form characteristic hydrochlorides.

The catechol derivatives of thiazole containing amino groupings thus far examined pharmacologically have shown a lower toxicity than adrenaline when injected into the albino rat intravenously and subcutaneously. Their toxicity appears to increase with the size of the molecule. Also they are rapidly absorbed when administered by the stomach and produce the same pharmacologic action as when injected intravenously or subcutaneously. Their relatively low toxicity and the absence of marked vasoconstricting, pathological lesions in the experimental animals indicate that their blood pressure raising action is not comparable with that of adrenaline. All the thiazoles of this series thus far examined have a definite analgesic and anesthetic action. This action apparently decreases with the size of the molecule. The preliminary pharmacological study of our thiazoles has been carried out in the laboratories of the donors of the Metz Fellowship,[3] and we desire to express here our appreciation of this cooperation.

Experimental Part

The thiazoles described in Table I were all prepared according to the general method by digestion of a thioamide with the required halogenated

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[1] Holder of the Metz Research Fellowship 1928–1929.

[2] Johnson and Gatewood, THIS JOURNAL, 51, 1815 (1929).

[3] Metz Research Laboratories in New York City.

ketone combination. The thioanisamide used was prepared according to the method of Rehländer,[4] and the anisonitrile synthesized as described by Hantzsch.[5] Demethylation of aromatic ether constructions to obtain the corresponding free phenols was accomplished by heating the thiazole with a 48% aqueous solution of hydrobromic acid, or by the action of the same reagent on the respective thiazole in glacial acetic acid.

Piperonylthio-amide, $CH_2O_2C_6H_3CSNH_2$.—This was obtained by heating the corresponding nitrile in an alcohol solution of ammonium sulfhydrate at 100°. The yield was 81% and the amide crystallized from alcohol in plates which melted at 180°.

Anal. Calcd. for $C_8H_7O_2NS$: N, 7.73. Found: N, 7.61, 7.64.

3,4-Dihydroxybenzonitrile, $(HO)_2C_6H_3CN$, was prepared from piperonylcyanide and phosphorus pentachloride;[6] yield, 75%.

3,4-Dihydroxythiobenzamide, $(HO)_2C_6H_3CSNH_2$.—This was prepared by addition of hydrogen sulfide to the above nitrile. The reaction takes place by heating in alcohol solution at 100°. The yield of crude thioamide was 80%. The compound crystallizes from hot water in the form of plates which melt at 153–154°. The water solution of the thiazole gives a deep green coloration when mixed with ferric chloride solution.

Anal. Calcd. for $C_7H_7O_2NS$: N, 8.28. Found: N, 8.10, 8.17.

TABLE I

NEW THIAZOLE COMPOUNDS

No.	Thiazole	Reagents		Yield, %
1	2-(*p*-Methoxyphenyl)-[a]	Bromo-acetal and thioanisamide		..
2	2-(*p*-Hydroxyphenyl)-[b]	Demethylation of 1 with 48% HBr		..
3	2-(*p*-Methoxyphenyl)-4-methyl-[b,c]	Chloro-acetone and thioanisamide		90
4	2-(p-Hydroxyphenyl)-4-methyl-	....		
5	2-(*p*-Methoxyphenyl)-4-(3,4-dihydroxyphenyl)-[d]	Chloro-acetocatechol and thioanisamide		..
6	2-(*p*-Hydroxyphenyl)-4-(3,4-dihydroxyphenyl)-[e]	....		
7	2-(3,4-Dihydroxyphenyl)-4-(3,4-dihydroxyphenyl)-[f]	Chloro-acetocatechol and	3,4-Dihydroxythiobenzamide	80
8	2-(3,4-Dihydroxyphenyl)-	Bromo-acetal and		..
9	2-(3,4-Dihydroxyphenyl)-4-methyl-	Chloro-acetone and		..
10	2-(3,4-Methylene-dihydroxyphenyl)-[g]	Bromo-acetal and	Piperonylthioamide	..
11	2-(3,4-Methylene-dihydroxyphenyl)-4-methyl-[h]	Chloro-acetone and		91
12	2-(3,4-Methylene-dihydroxyphenyl)-4-(3,4-dihydroxyphenyl)-[i]	Chloro-acetocatechol and		90

[a] B. p. 156–158° at 6 mm. [b] HCl salt contains one-half molecule of EtOH. [c] B. p. 168° at 7 mm. [d] Contains $2H_2O$ (10.54%). [e] Needles. Contains $2H_2O$ (11.35%). [f] Contains $1H_2O$ (6.1%). [g] Plates. [h] Needles from alcohol. HCl salt contains 1EtOH (4.64%). [i] Contains $2H_2O$, m. p. 135°.

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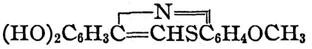
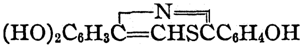
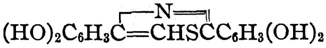
[4] Rehlander, Ber., 27,2159 (1894).

[5] Hantzsch, *ibid.*, **24**, 41 (1871).

[6] Ewins, J. *Chem. Soc.*, 95, 1487 (1909).

Table I *(Concluded)*

No.	Formula	Analyses, % N	Cl(HCl)	M. p., °C.	Hydrochloride Yield, %	M. p., °C.
1	 $\overset{\text{N}}{\text{CH=CHSCC}_6\text{H}_4\text{OCH}_3}$	7.24 7.25	15.5 ...	12–15	73 ..	167–169 .....
2	 $\overset{\text{N}}{\text{CH=CHSCC}_6\text{H}_4\text{OH}}$	7.82 7.82	14.92 ...	163–165	..	178–180
3	 $\overset{\text{N}}{\text{CH}_3\text{C=CHSCC}_6\text{H}_4\text{OCH}_3}$	6.86 6.76	12.60 13.42	57[a]	..	130–132
4	 $\overset{\text{N}}{\text{CH}_3\text{C=CHSCC}_6\text{H}_4\text{OH}}$	7.47 7.36	15.3 ...	220–221[b]	90	250–253
5	 $\overset{\text{N}}{(\text{HO})_2\text{C}_6\text{H}_3\text{C=CHSC}_6\text{H}_4\text{OCH}_3}$	4.61 4.66	10.42	154–155	..	106–208
6	 $\overset{\text{N}}{(\text{HO})_2\text{C}_6\text{H}_3\text{C=CHSCC}_6\text{H}_4\text{OH}}$	4.83 4.84	10.65 ...	212–213	..	.....
7	 $\overset{\text{N}}{(\text{HO})_2\text{C}_6\text{H}_3\text{C=CHSCC}_6\text{H}_3(\text{OH})_2}$	4.37 4.52	... ...	207	.. ..	....
8	 $\overset{\text{N}}{\text{CH=CHSCC}_6\text{H}_3(\text{OH})_2}$	7.39	...	181	..	215–218
9	 $\overset{\text{N}}{\text{CH}_3\text{C=CHSCC}_6\text{H}_3(\text{OH})_2}$	6.74	...	.....	..	250
10	 $\overset{\text{N}}{\text{CH=CHSCC}_6\text{H}_3\text{O}_2\text{CH}_2}$	6.69 6.73	14.23 14.36	84–85	..	216
11	 $\overset{\text{N}}{\text{CH}_3\text{C=CHSCC}_6\text{H}_3\text{O}_2\text{CH}_2}$	6.25 6.37	11.98 ...	94–95	....	
12	 $\overset{\text{N}}{(\text{HO})_2\text{C}_6\text{H}_3\text{C=CHSCC}_6\text{H}_3\text{O}_2\text{CH}_2}$	4.04 4.10	3.80 3.86	185[c]	..	212–216

[a] From petroleum ether. [b] From alcohol. [c] Anhydrous base.

Summary

1. Twelve new thiazoles containing aromatic groups in Positions 2 or 4 of the thiazole cycle have been synthesized.

2. The object of the work was to obtain aromatic combinations containing phenolic groups and especially the catechol derivatives, and to compare their pharmacological behavior with that of adrenaline.

3. All the compounds thus far studied have exhibited such marked physiological properties that the investigation of this series of compounds will be continued.

New Haven, Connecticut

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

ORGANIC COMPOUNDS OF SELENIUM. I. THE ACTION OF SELENIUM OXYCHLORIDE UPON KETONES

BY R. E. NELSON AND R. N. JONES

RECEIVED NOVEMBER 18, 1929 PUBLISHED APRIL 7, 1930

Selenium oxychloride is a very reactive compound and, therefore, lends itself readily to the syntheses of organic selenium compounds. Its activity may be classified under three headings, chlorination, oxidation and condensation.

The action of selenium oxychloride on paraffins, olefins, acetylenes, ethers, phenols, tertiary aromatic amines, Grignard's reagent, ketones and aromatic hydrocarbons has been described more or less thoroughly in the literature.[1]

In this investigation selenium oxychloride was allowed to act on the following ketones: acetone, acetophenone, propiophenone, *p*-chloro-acetophenone, methyl *p*-tolyl ketone, 2-methyl-5-isopropylacetophenone,methyl n-hexyl ketone, methyl ethyl ketone, diethyl ketone and benzophenone In general, the reaction can be represented by $2C_6H_5COCH_3 + OSeCl_2 \longrightarrow (C_6H_5COCH_2)_2SeCl_2 + H_2O$.

The reactions were carried out at room temperature with the exception of 2-methyl 5-isopropyl ketone. In this case the reaction was accelerated by heat.

The products were nearly insoluble in ether, benzene, petroleum ether and carbon tetrachloride. They were soluble in both water and alcohol with decomposition. No satisfactory method of recrystallization was found and it was necessary to remove impurities by first washing with benzene and then with ether.

Diethyl, methyl ethyl and methyl n-hexyl ketone reacted violently with the generation of heat and the evolution of hydrogen chloride. The solvent turned yellow, and then red, due to the decomposition of either the selenium oxychloride or a new product, but no solid separated.

The products of the action of selenium oxychloride on the ketones are more or less unstable, some beginning decomposition at once and others not showing marked decomposition for a period of two weeks. Decomposition gives a reddish sticky mass with strong lachrymatory action and an odor like that of chloro ketones.

Some dichloroselenomethylp-tolyl ketone was accidentally spilled on the investigator's hand. The skin became irritated and later formed slight

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[1] Morgan and Burstall, J. *Chem. Soc.*, 130,3260 (1928); Frick, THIS JOURNAL, 45, 1795 (1923); Mueller, *Chem.-Ztg.*, 43,843 (1919); Lenher, THIS JOURNAL. 43, 29 (1921); Kunckell, Ber., 28,609 (1795); Michaelisand Kunckell, *ibid.*, 30,2823 (1897); Kunckell and Zimmermann, Ann., 314, 281 (1901); Strecker and Willing, Ber., 48, 196 (1915); Godchaux, *ibid.*, 24, 765 (1891).

pockets that remained red for four days. Then the skin peeled off on the affected area as in the case of a sunburn.

Experimental

The ketones used in the experiments were obtained from the Eastman Kodak Company. The selenium oxychloride was obtained from the J. T. Baker Chemical Company and was not further purified.

In each case the reagents were added in the ratio of two moles of the ketone to one mole of the selenium oxychloride, Anhydrous ether was found to be the most satisfactory solvent in which to carry out the reactions. The mixture was rapidly stirred and usually in a few minutes a white solid separated with the generation of considerable heat.

The products were identified by analysis for selenium and chlorine and also by comparison with the literature in the case of known compounds.

Analysis for selenium[2] was carried out by fusion with potassium nitrate and sodium peroxide in a Parr bomb. The fused mass was dissolved, acidified with hydrochloric acid and the selenium precipitated by means of sulfur dioxide.

Analysis for chlorine was carried out in a similar way except that nitric acid was used for acidifying and silver chloride was precipitated by the addition of silver nitrate. The analyses indicate a certain amount of chlorination.

Table I summarizes the work carried out with the various ketones.

TABLE I

PREPARATIONAL DATA, PHYSICAL CONSTANTS AND ANALYSES

	Ketone	Seleno product	Formula
1	Acetone	Dichloroseleno-acetone	$(CH_3COCH_2)_2SeCl_2$
2	Acetophenone	Dichloroseleno-acetophenone	$(C_6H_5COCH_2)_2SeCl_2$
3	*p*-Chloro-acetophenone	Dichloroseleno-*p*-chloro-acetophenone	$(ClC_6H_4COCH_2)_2SeCl_2$
4	Propiophenone	Dichloroselenopropiophenone	$(C_6H_5COC_2H_4)_2SeCl_2$
5	Methyl p-tolyl ketone	Dichloroselenomethyl *p*-tolyl ketone	$(CH_3C_6H_4COCH_2)_2SeCl_2$
6	2-Methyl 5-isopropylacetophenone	Dichloroseleno-2-methyl-5-isopropylacetophenone	$[CH_3(C_3H_7)C_6H_3COCH_2]_2SeCl_2$

	M. p. °C.	Yield, %	Decomposition[a]	Selenium, %		Chlorine, %	
				Calcd.	Found	Calcd.	Found
1	81	77	3–4 Hours	29.98	29.98	26.84	27.19
2	121.5	77	1–2 Days	20.41	20.02	18.27	18.25
3	126	50	1–2 Weeks	17.33	17.35	31.03	31.02
4	118	60	2 Weeks	19.03	18.61	17.04	17.36
5	129	60	2 Weeks	19.03	18.00	17.04	17.49
6	133	50	2 Weeks	15.83	14.67	14.17	15.07

[a] Impurities apparently affect the stability considerably as different lots showed varying degrees of stability. Contact with an iron spatula frequently started decomposition at once.

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[2] Shaw and Reid, THIS JOURNAL, 49, 2330 (1927).

Methyl *n*-hexyl ketone, methyl ethyl ketone and diethyl ketone reacted violently but produced no solid and the products seemed to decompose as fast as they were formed.

Benzophenone was treated with selenium oxychloride in carbon disulfide solution in the presence of anhydrous aluminum chloride and heated for several days. Hydrogen chloride was given off slowly. After standing for two weeks, most of the solvent evaporated, leaving a crystalline mass. It was extracted with chloroform and on the evaporation of the chloroform crystals separated. They were placed on a porous plate but decomposed as soon as the protecting layer of chloroform evaporated.

Summary

1. The reaction between selenium oxychloride and certain ketones has been studied.
2. Condensation reactions took place between two molecules of the ketones and one molecule of selenium oxychloride.
3. New organic compounds of selenium have been prepared and studied.

WEST LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

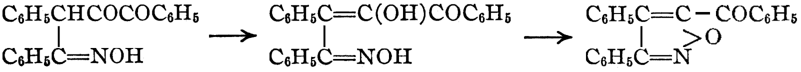
CYCLIC NITRONES

BY E. P. KOHLER AND C. R. ADDINALL

RECEIVED NOVEMBER 26, 1929 PUBLISHED APRIL 7, 1930

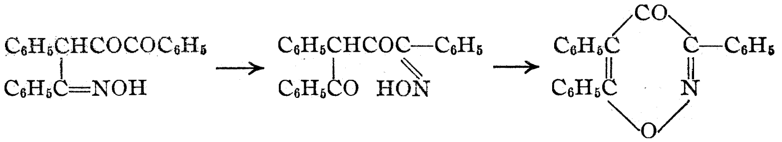
In earlier papers of this series there is mention of a "purple anhydride" which appeared in small quantities whenever solutions of triphenyl butane trione oxime became acid. Like benzoyl diphenyl isoxazole, previously investigated, this purple compound is a monomolecular anhydride of the oxime. It is, therefore, a surprisingly simple compound to have such a rich, deep purple color. This wide contrast between color and complexity was one of the reasons for the investigation.

Another incentive for investigating the purple compound arose from the difficulty of accounting for more than one monomolecular anhydride. The oxime is so constituted as to make an open-chained anhydride impossible, and the evidence is conclusive that the isoxazole derivative represents the anhydride of the only possible enolic modification of the open-chained oxime



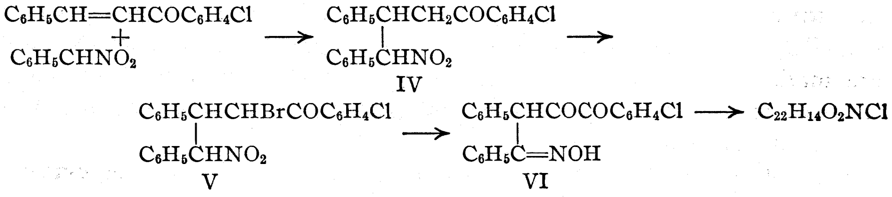
$$\begin{array}{l} C_6H_5CHCOCOC_6H_5 \\ \quad | \\ C_6H_5C{=}NOH \end{array} \longrightarrow \begin{array}{l} C_6H_5C{=}C(OH)COC_6H_5 \\ \quad | \\ C_6H_5C{=}NOH \end{array} \longrightarrow \begin{array}{l} C_6H_5C{=}C-COC_6H_5 \\ \quad | \qquad \quad >O \\ C_6H_5C{=}N \end{array}$$

In view of these facts it seemed probable that the formation of the purple compound is preceded by a rearrangement of the oxime. Since the slightest imaginable acidity leads to the appearance of the substance, a rearrangement involving the carbon chain is unlikely, but an interchange of the oximido group and the oxygen of a more active carbonyl is not improbable. A shift like this would be favored by an acid medium, and it would lead to a new anhydride

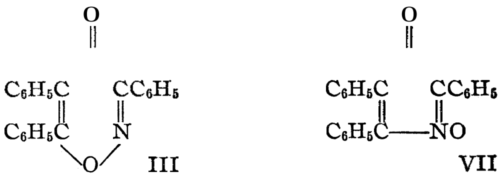


I II III

An attempt to determine by ozonization whether III is a possible formula for the purple anhydride failed because the products—benzoic acid and benzonitrile—are not sufficiently significant. In order to employ this method successfully it was necessary to secure an analogous compound in which either the a- or the y-phenyl group could be identified by a substituent. Such a compound was, therefore, prepared in accordance with the scheme



The ozonization products of this new purple compound were benzoic acid and pchlorobenzonitrile—products which showed conclusively that in these purple compounds the nitrogen is attached to the y-carbon, and which also reduced the number of plausible formulas to two



In order to get a basis for distinguishing between these two formulas, the purple compound was treated with methyl magnesium iodide in an apparatus with which it is possible to determine both the volume of any gas that may be evolved and the amount of reagent that is consumed by a given weight of substance.' It was found that one mole of the anhydride liberated one mole of gas and consumed about **3** moles of reagent. Since there seems to be no reason why an orthoxazine derivative like III should liberate gas from methyl magnesium iodide, while isoxazoline oxides invariably do so, this result is evidence for the nitrone formula VII.

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[1] Kohler, Stone and Fuson, THIS JOURNAL, 49,3181 (1927).

The reaction between methyl magnesium iodide and the purple compound supplied valuable information but the physical properties of the product made it unsuitable for further investigation. We, therefore, turned to phenyl magnesium bromide. Here a fresh difficulty arose. The product of the reaction between phenyl magnesium bromide and the purple anhydride is stable only in solid form. In solution it changes too rapidly for a reliable determination of its molecular weight; and by analyses alone it is not possible to determine how many molecules of the magnesium derivative are involved in the reaction. This difficulty was met by using bromo phenyl magnesium bromide in one experiment; a determination of bromine in the product showed that the reaction involves but one molecule of reagent for one of anhydride.

With this much established, we undertook to ascertain the mode of addition of the Grignard reagent by ozonization of the product, but found that it changed with sufficient rapidity to impair the value of the results. Cautious oxidation with chromic acid proved to be more helpful because, in addition to benzoic acid, it gave a substance which was identified as $C_6H_5COCOC(C_6H_5)_2OH$. These oxidation products, even though they are inadequate to establish the structure of the substance, nevertheless showed conclusively that the Grignard reaction does not consist in addition to a carbonyl group.

From the experiments that have been described it became evident that in order to use the Grignard reaction as a means of determining the structure of the purple compound, it was essential to stabilize the Grignard product before undertaking its degradation. It was, therefore, converted into its methyl ether. The ether is stable, easily obtained in a perfectly pure condition, and in every way admirably adapted for structural work. Its composition and molecular weight are represented by the formula $C_{29}H_{23}O_2N$, and its relation to the purple compound by the equation

$$C_{22}H_{15}O_2N + C_6H_6 + CH2 = C_{29}H_{23}O_2N$$

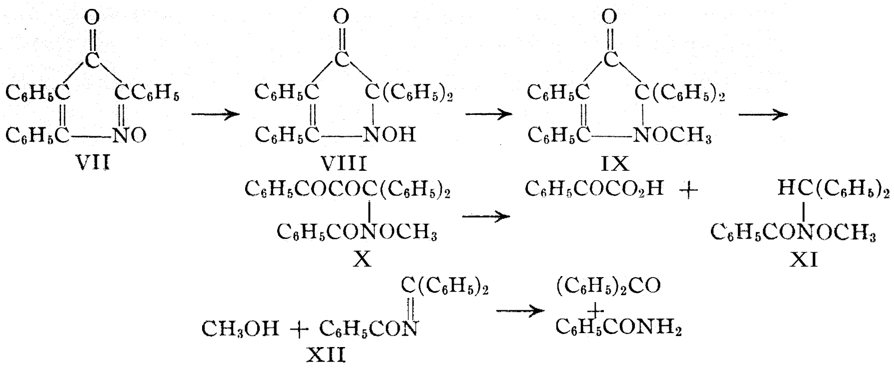
The ether is insensitive to both acids and bases. By very cautious oxidation with chromic acid it was possible to add two atoms of oxygen without disrupting the molecule—the oxygen atoms, doubtless, taking the place of a double linkage. The oxidation product was readily attacked by bases, which cleaved it smoothly into phenyl glyoxylic acid and a nitrogenous compound which contained the rest of the molecule

$$C_{29}H_{23}O_4N + H_2O \longrightarrow C_6H_5COCO_2H + C_{21}H_{19}O_2N$$

When the nitrogenous compound was heated above its melting point, it lost methyl alcohol, passing into a new nitrogen compound. This new product was hydrolyzed by acids to benzophenone and benzamide

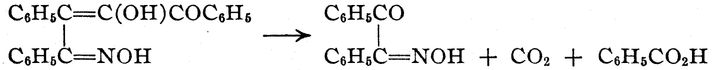
$$\text{I} \quad C_{21}H_{19}O_2N = C_{20}H_{15}ON + CH_3OH$$
$$\text{II} \quad C_{20}H_{15}ON + H_2O = (C_6H_5)_2CO + C_6H_5CONH_2$$

When all these facts are fitted together, they constitute a very complete proof that the purple anhydride is the cyclic nitrone VII



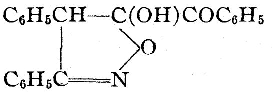
VII VIII IX X XI XII

Concerning the mechanism by which the purple compound is formed from the oxime, it is not possible as yet to speak with any confidence. The open-chained formula of the oxime is based largely on its oxidation to α-benzil monoxime by sodium peroxide

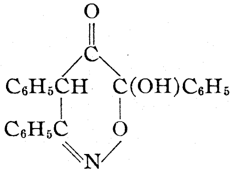


$$\begin{matrix} C_6H_5C{=}C(OH)COC_6H_5 \\ | \\ C_6H_5C{=}NOH \end{matrix} \longrightarrow \begin{matrix} C_6H_5CO \\ | \\ C_6H_5C{=}NOH \end{matrix} + CO_2 + C_6H_5CO_2H$$

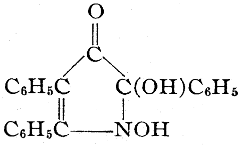
It would be difficult to reconcile these oxidation products with any other formula, but not a single open-chained derivative of the oxime is known. All reagents that do not disrupt the molecule transform the substance either into a cyclic isomer or into derivatives of cyclic isomers which belong to one of the following types



A

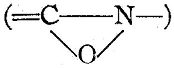


B

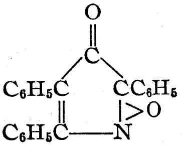


C

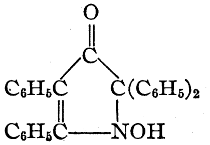
It is quite possible that all of these forms are present in solutions of this extremely active substance. If that be the case, then the formation of the purple nitrone merely represents the dehydration of the cyclic modification C.

In whatever manner the anhydride may be formed, it manifestly belongs to a varied class of substances which are of especial interest at present in connection with modern theories of valence—a class that includes the N-ethers of oximes, the isatogens, the aci-nitro compounds and their ethers, and the isoxazoline oxides. The formulas with a carbazoxy ring , which were formerly used extensively for representing these compounds, have now been generally abandoned in favor of those of the "nitrone" type $(>N{=}O)$, although they are still occasionally regarded as possible alternatives in special cases.[2] We regard the evidence against the ring formulas as conclusive; they cannot be reconciled with the spectrochemical results of Brady[3] and of Auwers and Ottens,[4] the values for the parachor found by Sugden,[5] and the color of the isatogens and of our anhydrides.[6]

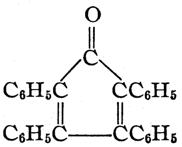
If these anhydrides had a carbazoxy ring (D), their color should not differ greatly from that of the addition products (E) all of which are yellow. Instead of this they have a very dark purple color which is scarcely distinguishable from that of Ziegler and Schnell's tetraphenyl cyclopentadienone (F.)[7]



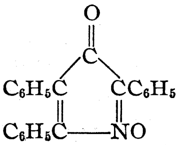
D



E

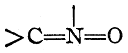


F



G

It is customary to represent the unsaturated system in nitrones with twinned double linkages analogous to those occurring in allenes, isocyanates and ketenes



$$>C{=}\overset{|}{N}{=}O \qquad >C{=}C{=}C< \qquad -N{=}C{=}O \qquad >C{=}C{=}O$$

The nitrones, however, not only bear but little resemblance to these other classes of unsaturated compounds, but also very rarely, if ever, form addition products in which the addends have taken the place of a double linkage. The list of substances which have been added to nitrones is both long and varied; it includes isocyanates,[8] organic magnesium compounds: alcohols,[10] acetic acid, acetyl chloride, acetic anhydride,[10b] benzoyl chloride,[11] and diphenyl ketene.[8d] In the addition products which the various nitrones form with all of these substances—except possibly

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[2] Staudinger and Miescher, *Helv. Chim. Acta,* 2, 554 (1919); Gabriel and Gerhard, *Ber.,* 54, 1073 (1921); Ruggli, *Helv. Chim. Acta,* 6,594 (1923).

[3] Brady, *J. Chem. Soc.,* 105,2104 (1914).

[4] Auwers and Ottens, *Ber.,* 57,446 (1924).

[5] Sugden, *J. Chem. Soc.,* 127, 1525 (1925).

[6] Pfeiffer, *Ann.,* 411, 72 (1916).

[7] Ziegler and Schnell, *ibid.,* 445,266 (1925).

[8] (a) Beckmann, *Ber.,* 23,3395 (1890); *(b)*27,1957 (1894); (c) Goldschmidt, *ibid.,* 24, 2808 (1891); (d) Staudinger and Miescher, *Helv. Chim. Acta,* 2, 554 (1919).

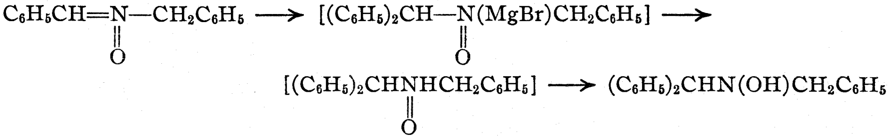
[9] Angeli, Alessandri and Aiazzi-Mancini, *Atti accad. Lincei, [V]*20, *I,* 546 (1911); Staudinger, *Helv. Chim. Acta,* 2, 554 (1919).

[10] (a) Heller, *Ber.,* 55, 474 (1922); (b) Ruggli, *ibid.,* 52, 5 (1919); (c) Ruggli, Bollinger and Leonhardt, *Helv. Chim. Acta,* 6,594 (1923).

[11] Wieland and Kitasato, *Ber.,* 62, 1251 (1929); *Ann.,* 475, 42 (1929).

diphenyl ketene—the addends are invariably found at the ends of the unsaturated system.

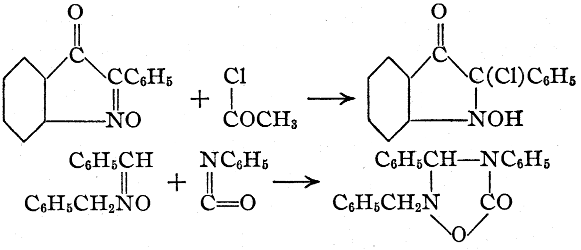
Thus, in a typical example, the addition of phenyl magnesium bromide to the N-benzyl ether of benzaldoxime leads to the formation of benzyl-diphenyl methyl-hydroxylamine. In order to reconcile this result with the usual nitrone formula, Angeli[12] made the assumption that the reaction involves both addition and rearrangement



$$C_6H_5CH{=}\underset{\overset{\|}{O}}{N}{-}CH_2C_6H_5 \longrightarrow [(C_6H_5)_2CH{-}\underset{\overset{\|}{O}}{N}(MgBr)CH_2C_6H_5] \longrightarrow$$

$$[(C_6H_5)_2CH\underset{\overset{\|}{O}}{N}HCH_2C_6H_5] \longrightarrow (C_6H_5)_2CHN(OH)CH_2C_6H_5$$

It is possible to account for the addition products that are obtained with alcohols and acetic acid in a similar manner, but not for those obtained with acid chlorides, acid anhydrides and phenyl isocyanide. Here the assumption that a 1,2-addition product would undergo rearrangement to a substance in which the addends are in the 1,3-position lacks all probability; the products must be due to 1,3-addition



From these examples it is evident that the unsaturated system in these nitrones is so constituted as to permit 1,3-addition and also that in every case in which it has been possible to establish the structure of the primary product, this has always been found to be a 1,3-addition product. There appears to be no good reason, therefore, for assuming a different mechanism in those cases in which 1,2-addition followed by rearrangement is conceivable; it seems much more probable that in substances of this type 1,3-addition is a normal process.

The customary method of representing the unsaturated system in nitrones neither suggests the possibility of 1,3-addition nor accounts for its occurrence. Moreover, the link between the nitrogen and the oxygen in these oxides certainly has nothing in common with that which is represented by the N=O group in nitroso compounds; it is of the type which has been called "semi-polar" or "coordinate." By resorting to electronic formulas it is easy to understand that 1,3-addition is possible in all systems in which such a "coordinate" link is twinned with a double linkage. Since

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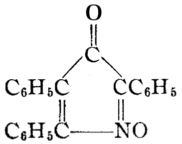
[12] Ref. 9 *a*, p. 548.

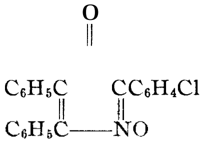
there is no accepted method for symbolizing such a coördinate link, we prefer to represent the unsaturated system in nitrones by $>C=\underset{|}{N}O$.[13]

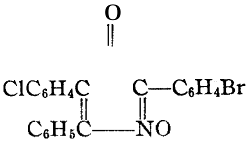
Experimental Part

Preparation of Materials

In the course of this investigation we studied three purple anhydrides


VII


XIII


XIV

The first of these substances was made from α, y, 6-triphenyl butanetrione oxime which was prepared in the manner described in earlier papers." In successful operations the crude dry product is sufficiently pure for nearly all purposes. When it is necessary to recrystallize it from acetone and ether it is essential to remove all trace of acid from the walls of the apparatus, to use only alcohol-free ether and acetone that has been distilled from permanganate and alkali, and to avoid contamination by acid in the air.

The second purple compound was made from the corresponding chlorinated oxime.[15] Inasmuch as the intermediates in the preparation of this oxime were obtained in the same manner as those employed in securing the halogen free oxime, it will be sufficient to tabulate their properties without describing the operations in detail.[16]

Substance	Melting point, °C.	Yield, %	Composition Calcd., % C	H	Found, % C	H
$\begin{array}{l}C_6H_5CHCH_2COC_6H_4Cl\\ \quad\vert\\ C_6H_5CHNO_2\end{array}$	176	93	69.6	4.7	69.0	4.9

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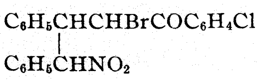
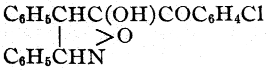
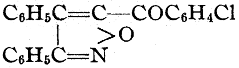
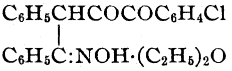
[13] The term "nitronic acid" which Bamberger [*Ber.*, 35, 54 (1902)] proposed as a substitute for aci-nitro compounds is unfortunate because it implies a much closer analogy to carbonic acids than actually exists [Kuhn and Albrecht, *ibid.*, 60, 1297 (1927)]. The term "nitrone" which was proposed by Pfeiffer for these unsaturated oxides seems almost equally unfortunate because, in reality, it is not the group $=\underset{|}{N}O$ but the entire unsaturated system $>C=\underset{|}{N}O$ that is equivalent to $>C=O$. And if the termination —nitrone— is to include this entire system, then it becomes extremely difficult to name individual substances. We have, therefore, used the term nitrone only as a general designation for all classes of substances that contain the unsaturated system $>C=\underset{|}{N}O$ and have named the individual substances as oxides.

[14] (a) Kohler, THIS JOURNAL, 46, 1733 (1924); (b) 47, 3030 (1925).

[15] G. H. Reid, "Dissertation," Harvard University, 1926.

[16] All experiments with the p-chloro compound, including the preparation af the purple compound and its ozonization, were performed by G. H. Reid.

Substance	Melting point, °C.	Yield, %	Composition Calcd., % C	H	Found, % C	H
 $\begin{array}{l}C_6H_5CHCHBrCOC_6H_4Cl\\ \mid\\ C_6H_5CHNO_2\end{array}$	178	95	57.8	3.7	57.6	3.8
 $\begin{array}{l}C_6H_5CHC(OH)COC_6H_4Cl\\ \mid \quad >O\\ C_6H_5CHN\end{array}$	165	75	69.9	4.2	69.7	4.5
 $\begin{array}{l}C_6H_5C{=}C{-}COC_6H_4Cl\\ \mid \quad >O\\ C_6H_5C{=}N\end{array}$	164	75	73.2	3.7	73.2	4.1
 $\begin{array}{l}C_6H_5CHCOCOC_6H_4Cl\\ \mid\\ C_6H_5C{:}NOH\cdot(C_2H_5)_2O\end{array}$	112(eff.)	80	Cl 7.8		Cl 7.9	

In the preparation of the third purple compound from *p*-bromobenzal *p*-chloro-acetophenone, the sequence of reactions was the same as in the preceding cases, but none of the intermediates were purified or analyzed.

The Purple Compounds

For transforming the pure oximes into the purple compounds we found no better method than that mentioned in an earlier paper[17]—the action of hydrogen chloride on a solution of the oxime in chloroform. The procedure is as follows. The oxime is dissolved in chloroform which has previously been freed from alcohol, dried with phosphorus pentoxide, and saturated with dry hydrogen chloride. The solution immediately becomes purple in color and water soon collects in drops. It is saturated afresh with hydrogen chloride, which is passed through it for five minutes, then poured into a shallow dish and allowed to evaporate. To remove the last of the chloroform, the residue is mixed with dry ether, which is likewise allowed to evaporate. The residue is then collected on a filter and thoroughly washed with dry methyl alcohol, which removes the hydroxy isoxazoline **(A)** and leaves the purple compound. Pure oximes pass quantitatively into these two types of compound and these substances are formed in the proportion of 70–75% of purple anhydride to 25–30% of hydroxyl compound. When other substances turn up in the process, they are present in the oxime or due to other impurities in it.

This procedure is applicable to the crude oxime unless, owing to faulty operation, it is excessively impure. In that case, it is better to substitute phosphorus pentoxide for the hydrogen chloride. Thus the chloro bromo-oxime could not be obtained in crystalline form and, therefore, could not be freed from ether-soluble impurities; but pure anhydride was obtained from it by the following procedure.

The yellow paste obtained by treating 15 g. of α-bromo compound with alkalies in the usual manner was dissolved in a minimum of hot dry alcohol-free chloroform which was heated on a steam-bath. To the boiling solution phosphorus pentoxide was added until the mixture had a uniform purple color-about 2 g was necessary. The chloroform was boiled off and the solid mass was repeatedly extracted with boiling water. In order to remove a high-melting yellow impurity, the crude product was dissolved in boiling benzene, the solution filtered and evaporated to dryness The residue was freed from hydroxy isoxazoline by extraction with methyl alcohol, and finally recrystallized from chloroform and petroleum ether; yield, **7** g.

The three purple compounds resemble one another very closely; they crystallize well, melt without decomposition at a high temperature, are sparingly soluble in ether and in

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[17] Ref. 14 b, p. **3033.**

the lower alcohols, and are readily soluble in acetone, in chloroform, in ethyl acetate and in boiling benzene. The color of the solutions is remarkably like that of a concentrated solution of potassium permanganate.

3-Keto-2,4,5-triphenyl Pyrrolenine Oxide, VII.—The unhalogenated oxide crystallizes in double pyramids and melts at 175–177°.

Anal. Calcd. for $C_{22}H_{15}O_2N$: C, 81.2; H, 4.7; mol. wt. 325. Found: C, 81.1; H, 4.8; mol. wt. 330.

In the "machine"[18] one mole of the substance liberated 0.9 mole of gas and consumed 3.3 moles of reagent.

3-Keto-2-(4-chlorophenyl)-4,5-diphenyl Pyrrolenine Oxide, XIII.—The chloro anhydride crystallizes in stout needles and melts at 201°.

Anal. Calcd. for $C_{22}H_{14}O_2NCl$: C, 73.3; H, 3 9; mol wt, 360. Found: C, 73 5; H, 3.8; mol. wt., 327.

3-Keto-2-(4-bromophenyl)-4-(4-chlorophenyl)-5-phenyl Pyrrolenine Oxide, XIV.—The chloro-bromo oxide crystallizes in very minute prisms and begins to sinter at 180°.

Anal. Calcd. for $C_{22}H_{13}O_2NClBr$: C, 60.1; H, 3.0. Found: C, 60.0; H, 3.4.

Ozonization

A current of ozonized oxygen containing about 6% of ozone was passed through a Suspension of 10 g. of the unhalogenated anhydride. Ozone appeared in the effluent gas immediately, but the solid gradually dissolved and the purple color then began to fade. It disappeared completely after eight hours, leaving a colorless paste suspended in a pale yellow solution. The paste disappeared when the mixture was shaken with water. Tests for aldehydes and for phenyl glyoxylic acid in the resulting solution were negative. The solution was, therefore, freed from chloroform, the residual paste dissolved in ether, the ethereal solution dried and evaporated. It left a pale yellow paste with a strong odor of benzonitrile. A portion that was heated on the steam-bath first gave off benzonitrile, which was turned into benzamide for identification, and then a sublimate of benzoic acid. All attempts to isolate a solid product from the oil were unsuccessful. When left to itself it very slowly but persistently turned into benzonitrile and benzoic acid.

Three grams of *p*-chloro oxide when ozonized in the same manner gave a similar result, the only difference being that instead of benzonitrile, one of the products was p-chlorobenzonitrile. This melted at 94° and addition of an authentic sample caused no depression of the melting point.

Reaction with Grignard Reagents

Since the anhydrides are very sparingly soluble and the Grignard products both sensitive and difficult to purify, it is important to start with pure materials, use a large excess of Grignard reagent, and operate as rapidly as possible. As a result of many experiments we adopted the following procedure.

A solution of phenylmagnesium bromide, made from 4 g. of magnesium in a 1-liter flask that is provided with an effective stirrer, is cooled in ice water. To this solution is added, rapidly and with vigorous stirring, a solution of 10 g. of the anhydride in 100 cc. of hot benzene. The purple color should disappear immediately. After ten minutes, the flask—which, depending upon the relative quantities of ether and benzene, may contain either a clear yellow solution or a suspension of solution and yellow paste—is cooled in a freezing mixture. The solution is then diluted with 400-500 cc. of cooled, low-boiling

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[18] Kohler, Stone and Fuson, THIS JOURNAL, 49, 3181 (1927).

petroleum ether, which completes the precipitation of the pasty, yellow magnesium derivative.

After adequate dilution with petroleum ether, the solution is nearly colorless and contains nothing of value and hence is discarded; the yellow paste is composed mainly of addition product but contains a small quantity of phenyl magnesium bromide and other impurities. After the addition of 100 cc. of ether, it may be decomposed either with iced hydrochloric acid or with ammonium chloride. When it is decomposed with iced acid the result is a lemon-yellow ethereal solution which immediately begins to deposit yellow crystals of the magnesium-free product; yield of crude dry product, about 85%.

When the yellow pasty magnesium compound is decomposed with 30 g. of ammonium chloride, it usually forms a crystalline ammonium compound which is insoluble in ether and in ammonium chloride solution. This compound is stable in the presence of ammonia, but it rapidly turns green after it has been washed with water and ether.

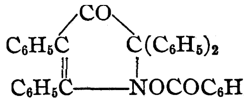
1-Hydroxy-2,2,4,5-tetraphenyl Pyrrolidone-3, **VIII.**—The pure dry Grignard product appears to be perfectly stable, but the crude material slowly turns green and all solutions of the substance, even those made by dissolving perfectly pure material likewise become green. This change of color takes place in the absence of air, but access of air appears to promote it. It takes place more rapidly in benzene than in acetone and more rapidly in the latter than in ether, and it is promoted by increase in temperature. Since the substance is sparingly soluble in ether, it is best to purify it by dissolving it in the minimum quantity of warm acetone and immediately diluting the solution with cold anhydrous ether. It is thus obtained in yellow plates or prisms that usually have a greenish cast.

Anal. Calcd. for $C_{28}H_{21}O_2N$: C, 83.3; H, 5.2. Found: C, 83.4; H, 5.8.

Molecular weight determinations gave values ranging from nearly 800 in freezing benzene to 735 in dioxane. Since all solutions had turned to a vivid green during the operations, the significance of these values is uncertain. In a capillary tube the substance melts to a green liquid at about 184°, and shortly thereafter gives off a little gas as the melt resolidifies to a yellow solid. This high-melting, very sparingly soluble solid also constitutes the final product of the changes that occur in solution.

Oxidation with **Permanganate.**—A solution of the Grignard product in acetone, on treatment with potassium permanganate, first turned dark green in color and then became colorless. The acetone solutions, when manipulated in the usual manner, yielded a small quantity of a solid melting at 163°, benzoic acid and benzophenone.

Oxidation with Chromic Acid.—A solution of 4 g. of the Grignard product in 100 g. of hot glacial acetic acid was treated, gradually, with a solution of chromic acid that was made by dissolving 4 g. of the anhydride in 4 cc. of water and diluting with 10 g. of glacial acetic acid. Each addition of the oxidizer produced a dark green color which rapidly disappeared on shaking. When further addition no longer affected the color, the solution was cooled and poured into water. The resulting suspension was filtered, the pasty solid thoroughly washed with water, and then dissolved in ether. From the ethereal solution sodium carbonate extracted approximately one equivalent of benzoic acid. The dried, acid-free ethereal solution on evaporation left a yellow oil that partially solidified when rubbed with methyl alcohol. The solid was identified as $C_6H_5COCOC(C_6H_5)_2$-OH by comparison with a sample on hand.[19]

The Benzoate of the Grignard Product,  .—As a first attempt at stabilizing the Grignard product we turned it into the benzoate. Sodium

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[19] Kohler, This Journal, 47,3036 (1925).

hydroxide converts the hydroxyl compound into a crystalline yellow sodium salt which is rapidly hydrolyzed by water but is stable in 5% sodium hydroxide solution. This sodium salt reacts with benzoyl chloride to form the benzoate but the yield is poor. Better results were obtained with pyridine. To a solution of 2 g. of the substance in hot dry pyridine was added 2 g. of benzoyl chloride. The mixture was set aside for eighteen hours, during which it deposited 1.3 g. of large greenish-yellow crystals. By recrystallization from boiling benzene the product was obtained in colorless rhomboidal plates, sparingly soluble in ether and in alcohol, and melting at 225°. From the benzene the benzoate crystallized with a molecule of solvent.

Anal. Calcd. for $C_{35}H_{25}O_3N\cdot C_6H_6$: C, 84.1; H, 5.3. Found: C, 84.0; H, 5.0.

The molecular weight which in boiling benzene was found to be 542 instead of 507 calcd. indicated that the Grignard product was monomolecular, but beyond this the benzoate was useless for our purpose.

The Methyl Ethers and Their Degradation

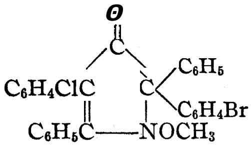
The yellow sodium salt of the Grignard product reacts readily with dimethyl sulfate and forms the corresponding methyl ether in almost the calculated quantity. The most satisfactory method of getting this ether is as follows.

The solution obtained in the Grignard reaction is transferred to a separating funnel in which it is cooled and diluted with petroleum ether. After decanting the petroleum ether layer and adding ordinary ether, the pasty yellow magnesium derivative is decomposed with iced hydrochloric acid in the usual manner. The aqueous layer is drawn off, the ethereal layer washed with water and then immediately shaken with excess of 10% sodium hydroxide. The crystalline yellow sodium compound thus formed is collected on a sintered glass suction funnel and washed with ether and with 5% sodium hydroxide.

The relatively pure sodium salt thus obtained is transferred immediately to a flask containing 150 cc. of 3% sodium hydroxide and treated with 15 g. of dimethyl sulfate. This gradually transforms it first to an oil and then to a solid. After decomposing the excess of dimethyl sulfate by warming on a steam-bath, the solid is collected in a funnel, thoroughly washed with hot water and dried. The yield of crude dry product is 13 g. The ether is readily purified by recrystallization from acetone and methyl alcohol; yield, 12.2 g. of pure ether from 10 g. of the purple anhydride.

Anal. Calcd. for $C_{29}H_{23}O_2N$: C, 83.5; H, 5.6; OCH_3, 7.4; mol. wt., 417. Found: C, 83.3; H, 5.8; OCH_3, 6.0; mol. wt., 416.

The methyl ether is moderately soluble in ether and in methyl alcohol, readily soluble in acetone and in chloroform. Its solutions in all solvents are deep yellow but it crystallizes in needles that are all but colorless. It melts at about 185°, with effervescence due to loss of formaldehyde, then resolidifies to the same waxy solid that is formed by melting the hydroxyl compound.



1-Methoxy-2(**4-bromophenyl**)-**4**-(**4-chlorophenyl**)-**2,5-di**-phenyl Pyrrofidone-3.—When the dihalogenated purple compound (XIV) was treated with phenyl magnesium bromide, it yielded a product very similar to that obtained from the halogen-free compound.

Anal. Calcd. for $C_{28}H_{19}O_2NBrCl$: C, 65.0; H, 3.7. Found: C, 65.6; H, 3.7.

The methyl ether, made like the corresponding halogen-free compound, crystallizes in very pale yellow needles and melts with decomposition at about 158°. In all common organic solvents it is more soluble than the unhalogenated ether.

Anal. Calcd. for $C_{29}H_{21}O_2NClBr$: C, 65.5; H, 4.0; OCH_3, 5.8. Found: C, 65.4; H, 4.1; OCH_3, 5.3.

Ozonization.—A current of ozonized oxygen was passed through a suspension of 5 g. of the unhalogenated ether in ethyl bromide for six hours, during which time all of the ether dissolved. Water was added to the clear pale yellow solution and the solvent was evaporated in a current of air. The residual yellow paste was distilled with steam until only a discolored film remained in the flask. The distillate was extracted and the contents of the ethereal solution were separated into acidic and indifferent components. The acidic portion gave 2 g. of pure benzoic acid. The non-acid portion was left, on evaporation of the ether, as a pale yellow oil which partially solidified when rubbed with methyl alcohol.

The composition, melting point (60°) and the hydrolysis products indicated that the solid was the methyl ether of benzophenoneoxime. The identification was completed by comparing the substance with a sample of this ether which was obtained by methylating the oxime with dimethyl sulfate. The formation of this uncommon type of ozonization product showed that the methyl ether contains the group $—C(C_6H_5)_2—N(OCH_3)—$ and, therefore, that the phenyl group of the Grignard reagent enters the 2-position.

Oxidation with Chromic Acid, X.—Three 5-g. lots of the ether were dissolved, separately, in 100 cc. of glacial acetic acid at 90°. To each solution 3 g. of chromic anhydride, dissolved in 3 cc. of water and 10 cc. of glacial acetic acid, was added as rapidly as the initial precipitate could be made to disappear by vigorous shaking. Each solution was then immediately poured into 500 cc. of cold water. The resulting suspensions were filtered, and pasty precipitates washed and dissolved in ether. The ethereal solutions were extracted with bicarbonate until free from acetic acid, then dried and concentrated to small volume. They gradually deposited 12 g. of crude solid oxidation product.

The crude oxidation product is not easy to handle because it decomposes in high-boiling solvents, and it both dissolves in and separates from low-boiling solvents very slowly. It is best to purify it partially by dissolving it in ethyl bromide, boiling down the solution until it begins to separate, and then completing the precipitation by diluting with an equal volume of ether. After filtering and washing with ether, the fine yellow powder can now be dissolved by prolonged boiling with 50 times its weight of dry methyl alcohol. On cooling, this solution very slowly deposits the pure oxidation product in transparent yellow needles, which melt at 160° and lose formaldehyde at about 175°.

Anal. Calcd. for $C_{29}H_{23}O_4N$: C, 77.5; H, 5.1; OCH_3, 7.0. Found: C, 77.5; H, 5.1; OCH_3, 8.4.

Oxidation of the Halogenated Ether, $ClC_6H_4COCOC(C_6H_5)(C_6H_4Br)N(OCH_3)-COC_6H_5$.—The chloro-bromo ether on oxidation with chromic acid gave a diketone which was much more easily purified. It crystallized in transparent yellow needles and melted with loss of formaldehyde at about 170°.

Anal. Calcd. for $C_{29}H_{21}O_4NBrCl$: C, 61.8; H, 3.8. Found: C, 61.8; H, 3.9.

Action of Sodium Methylate on the Oxidation Products.—Seven grams of the finely ground halogen-free oxidation product was shaken with a cold solution of 4 g. of sodium in 175 cc. of methyl alcohol until all but a few coarse particles had dissolved. The colorless solution was then evaporated as rapidly as possible in a strong draught. The moist pasty solid residue was collected on a funnel, washed with water until free from alkali and then repeatedly with low-boiling petroleum ether.

A weighed portion of the aqueous solution was acidified with dilute hydrochloric acid and then warmed with an excess of phenylhydrazine hydrochloride. It deposited the phenyl hydrazone of phenyl-glyoxylic acid, which was identified by comparison with a sample on hand. The weight of the hydrazone obtained was equivalent to 3 g. in place of 3.7 g. possible from 7 g. of oxidation product.

The solid product weighed 4.2 g. By a tedious series of operations, partly mechanical, it was finally separated into 1.5 g. of a substance that melted, with effervescence, at 155–160°, 2.0 g. of a substance melting at 115°, and a small quantity of a third product that crystallized in fine silky needles, sparingly soluble in ether, and melting without decomposition at 165°.

Diphenylmethenyl Benzamide, **XII.**—The lowest melting cleavage product (115°) is readily soluble in all common organic solvents except low-boiling petroleum ether. It crystallizes in large colorless prisms.

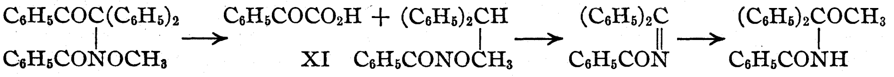
Anal. Calcd. for $C_{20}H_{15}ON$: C, 84.2; H, 5.3. Found: C, 84.0; H, 5.3.

The structure of this product was established by hydrolysis. The finely powdered substance dissolved readily in concentrated hydrochloric acid, forming a solution that almost at once became cloudy. Then the solution was diluted at this point and immediately extracted with ether; the ethereal layer contained benzophenone and benzamide, which were easily separated by evaporation to dryness and extraction with petroleum ether. Both substances were identified by comparison with authentic samples. When the acid solution was allowed to stand for some time before extraction, the products were benzophenone, benzoic acid and ammonium chloride.

The cleavage product that melts with effervescence at 155–160° is sparingly soluble in ether, moderately soluble in methyl alcohol and crystallizes in needles.

And. Calcd. for $C_{21}H_{19}O_2N$: C, 79.5; H, 6.0. Pound: C, 79.4; H, 5 9.

The relation between this substance and diphenylmethyl benzamide is clear, because the effervescence above the melting point is due to evolution of methyl alcohol and the residue left after heating is the benzamide derivative. The detailed structure of the substance is, however, uncertain because, while it appears to be a direct cleavage product of the diketonic compound, it may none the less be an isomer formed by addition of sodium methylate to the unsaturated benzamide derivative



$$\begin{array}{ccccccc} C_6H_5COC(C_6H_5)_2 & & C_6H_5COCO_2H + (C_6H_5)_2CH & & (C_6H_5)_2C & & (C_6H_5)_2COCH_3 \\ | & \longrightarrow & | & \longrightarrow & \| & \longrightarrow & | \\ C_6H_5CONOCH_3 & & \text{XI} \quad C_6H_5CONOCH_3 & & C_6H_5CON & & C_6H_5CONH \end{array}$$

In the absence of any conclusive evidence we have tentatively formulated the substance as the cleavage product XI.

Cleavage of the Halogenated Oxidation Product.—A suspension of 1.8 g. of the finely powdered oxidation product in a cold solution of 1 g. of sodium in 25 cc. of dry methyl alcohol was shaken for three hours, during which time the powder was replaced by a mass of fine white needles. The mixture was cooled in a freezing bath, the solid collected on a filter, washed with water and with chilled methyl alcohol, and dried in the air; yield, 1.3 g. This solid cleavage product—$(C_6H_5)Br(C_6H_4)CHN(COC_6H_5)OCH_3$—is sparingly soluble in ether and in methyl alcohol, more readily soluble in acetone. It crystallizes in fine needles and begins to effervesce freely at about 140°.

Anal. Calcd. for $C_{21}H_{18}O_2NBr$: C, 63.4; H, 4.5. Pound: C, 63.6; H, 5.1.

The Phenylhydrazone of 4-Chlorophenyl Glyoxylic Acid, $ClC_6H_4C(NNHC_6H_5)$-$COOH$.—The filtrates and washings from the solid cleavage product were combined and concentrated under diminished pressure at the ordinary temperature. The concentrated solution was thoroughly extracted with ether, then barely acidified with dilute acid. It deposited a sodium salt which was readily soluble in water, sparingly soluble in a saturated solution of sodium carbonate and crystallized in colorless plates. A solution of a small quantity of this salt was treated with phenylhydrazine hydrochloride. It promptly precipitated a lemon-yellow hydrazone which contained halogen. The hydrazone was recrystallized from aqueous methyl alcohol, from which it separated in needles melting at 188°.

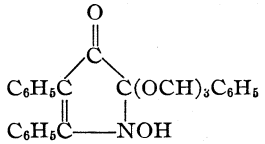
Anal. Calcd. for $C_{14}H_{11}O_2NCl$: C, 61.1; H. 4.0. Found: C, 61.2; H, 4.5.

Phenyl-(4-bromophenyl)-methenyl Benzamide, $(C_6H_5)(C_6H_4Br)C{=}NCOC_6H_5$.—The solid cleavage product begins to lose methyl alcohol below 140° but in order to get complete transformation it is necessary to heat it at a much higher temperature. Thus the residue left after heating 1.2 g. for ten minutes to 180–190° and then five minutes longer at 200° still contained some unchanged cleavage product which appeared after repeated extractions with low-boiling petroleum ether. The extracts deposited the unsaturated compound in small lustrous rhombs, readily soluble in organic solvents including petroleum ether.

Anal. Calcd. for $C_{20}H_{14}ONBr$: C, 65.9; H, 3.9. Found: C, 65.8; H, 3.9.

When the substance was hydrolyzed with concentrated hydrochloric acid, it gave *p*-bromobenzophenone and benzamide—both identified by comparison with authentic samples.

The 1,3-addition reactions of nitrones are evidently subject to the same kind of hindrance as the 1,4-addition reactions of α,β-unsaturated ketones. For while the N-phenyl and N-benzyl ethers of diphenyl acetaldoxime no longer combine either with Grignard reagents or with alcoholates, these purple nitrones, although equally highly substituted, still combine readily with both. The methyl alcohol addition product—obtained by adding sodium methylate and acidifying—closely resembles the Grignard product in color and instability. Like the Grignard product also, it readily forms a very stable methyl ether. There seems to be no doubt, therefore, that the addition product and its ether are constituted like the corresponding Grignard products.



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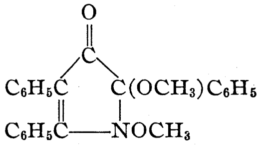

XVI

Addition of Sodium Methylate to the Nitrone.—Six grams of the purple nitrone was dissolved in a warm solution of 1 g. of sodium in 130 cc. of dry methyl alcohol. Through the brilliant scarlet solution a current of sulfur dioxide was passed until the color changed to pale yellow. The excess of sulfur dioxide was swept out with a current of air and the slight remaining acidity neutralized with methyl alcoholic ammonia. The solution was then concentrated and finally allowed to crystallize by slow evaporation. It deposited 6 g. of a fine yellow powder. This powder was recrystallized from acetone, from which it separated in large greenish octahedra resembling the Grignard product.

Anal. Calcd. for $C_{23}H_{19}O_3N$: C, 77.3; H, 5.3; OCH_3, 8.7; mol. wt., 357. Found: C, 77.6; H, 5.6; OCH_3, 8.7; mol. wt., 360.

1-Hydroxy-2-methoxy-2,4,5-triphenyl Pyrrolidone-3 (XV).—The methyl alcohol addition product is soluble in all common solvents except petroleum ether. It melts with decomposition at 163–165°. Like the Grignard product it is sufficiently acidic to dissolve in aqueous ammonia and aqueous alkalies. The solutions have the same scarlet color as those obtained by dissolving the nitrone in methyl alcoholic sodium methylate.

The Methyl Ether, XVI.—A solution of 10 g. of the methyl alcohol addition product in 100 cc. of 10% potassium hydroxide to which had been added 200 cc. of methyl alcohol was cleared by filtration, then treated with 10 g. of methyl iodide and set aside until the scarlet color had disappeared. The pale yellow solution thus formed was extracted with ether, the ethereal solution dried over sodium sulfate and allowed to evaporate. It deposited a mixture of yellow needles and a pale yellow high-melting powder.

The yellow needles were extracted with cold acetone and ultimately purified by recrystallization from ether. Like the methyl ether of the Grignard product, this methyl ether of the methyl alcohol addition product loses formaldehyde at the melting point, 175–180°.

Anal. Calcd. for $C_{24}H_{21}O_3N$: C, 77.6; H, 5.7; OCH_3, 16.7. Found: C, 77.3; H, 5.8; OCH_3, 14.5.

Summary

1. The preparation of three purple anhydrides from the corresponding oximes is described.

2. These remarkably colored substances are shown to be highly phenylated pyrrolenine oxides—capable of addition to the $>C=\underset{|}{N}O$ system.

3. The mode of addition with Grignard reagents to these compounds is studied and an analogous addition reaction with sodium methylate is reported.

4. The evidence in favor of a "nitrone" formulation as against the carbazoxy ring structure is summarized, support for the former proceeding from this study of the purple anhydrides.

5. The use of the term "nitrone" and the method of representing the unsaturated system in nitrones are discussed, preference being given to $>C=\underset{|}{N}O$.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING OF IOWA STATE COLLEGE]

A DELICATE COLOR TEST FOR MICHLER'S KETONE AND A LESS SENSITIVE TEST FOR PHOSGENE AND DIALKYLANILINES

BY HENRY GILMAN, O. R. SWEENEY AND L. L. HECK

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Introduction

The delicate color test of Gilman, Schulze and Heck[1] for reactive organometallic compounds, involving as it does the use of Michler's ketone, suggested its application as a test for Michler's ketone, and for phosgene, which is used in the preparation of the ketone. The test, which has found its widest application with organomagnesium compounds, is readily carried out by adding a very small quantity of the reactive organometallic com-

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[1] *(a)* Gilman and Schulze, THIS JOURNAL, 47, 2002 (1925); *Bull. soc. chim.*, [4] 41, 1479 (1927); (b) Gilman and Heck, *Rec. trav. chim.*, *48*, 193 (1929); (c) Gilman and Heck, *Ber.*, 62, 1379 (1929).

pound to Michler's ketone in benzene, hydrolyzing and then developing the color with a glacial acetic acid solution of iodine.

The limiting sensitivity for phosgene depends obviously on the delicacy of the test for Michler's ketone. It was first shown, in the present study, that it is possible to get a positive test with 1 cc. of Michler's ketone in a benzene solution which is 0.00001 molar, by means of a 2.25 molar solution of phenylmagnesium bromide. If it were possible to cause phosgene to react quantitatively with dimethylaniline, as follows

$$COCl_2 + 2(CH_3)_2NC_6H_5 \longrightarrow ((CH_3)_2NC_6H_4)_2C{=}O \qquad (I)$$

to give Michler's ketone, then it would be possible to get a positive test for a quantity as small as 0.000001 g. of phosgene. This order of sensitivity would be admirably suited for detecting less than toxic doses of phosgene.[2]

The possibility of getting a complete reaction between phosgene and dimethylaniline was rendered somewhat remote by the observation of Dyson[3] that "phosgene reacts very reluctantly with aromatic tertiary amines save in the presence of anhydrous aluminum chloride." However, we found that there is a significant reaction between phosgene and dialkylanilines under ordinary conditions and in the absence of aluminum chloride. Unfortunately, the reaction is not quantitative. It is possible to get a positive test with a 0.202 molar solution of phosgene in benzene, a degree of sensitiveness which is quite inadequate.[4] This concentration of phosgene is obviously not a limit for the detection by this method of the several dialkylanilines investigated, inasmuch as increasing concentrations of phosgene should favor the formation of ketone from the dialkylanilines. It was also found that tetraethyldiaminobenzophenone, $((C_2H_5)_2NC_6H_4)_2$-CO, has no advantage over Michler's ketone in the detection of reactive organometallic compounds.

Experimental Part

Michler's Ketone.—The Michler's ketone solutions were prepared by dissolving 0.2682 g. (0.001 mole) of ketone in 100 cc. of dry benzene and by dissolving a like weight in 100 cc. of freshly distilled dimethylaniline. These stock solutions were progressively diluted with benzene and dimethylaniline, respectively, until no positive color test was obtained. A positive test was obtained with 1 cc. of a 0.00001 molar solution of

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[2] Konowalow, Z. *ges Schiess-Sprengstoffw.*, 22,152 (1927), [*C. A.*, 21,4033 (1927)], has shown that a concentration of 0.0003 g. of phosgene in a liter of air is toxic to animals. On this basis 3 cc. of such an air mixture would be adequate for a positive test, providing the phosgene could be made to react quantitatively with dimethylaniline.

[3] Dyson, *Chemical Reviews*, 4, 109 (1927), has recently reviewed the chemistry of phosgene. See particularly p. 147.

[4] Admittedly there is the probability that a further study of the reaction between phosgene and dialkylanilines might result in a more complete reaction. It is doubtful if other noxious gases would interfere with the test because they would be destroyed by the subsequent addition of an excess of Grignard reagent or other reactive organometallic compounds.

the ketone in benzene, and with 1 cc. of a 0.000045 molar solution of the ketone in dimethylaniline. The test was carried out in the customary manner with 1 cc. of a 2.25 molar solution of phenylmagnesium bromide. Hydrolysis was effected by 3 cc. of water after the original mixtures were shaken for a moment at room temperature to effect intimate mixing. As the solutions became more dilute, it was necessary to add 2 cc. of glacial acetic acid containing just enough iodine to give the acetic acid a light brown color. With these low concentrations the appearance of color in only the water layer was taken as an indication of a weak but positive test.

Tetraethyldiaminobenzophenone.[5]—The test solutions of tetraethyldiaminobenzophenone were prepared by dissolving the freshly purified ketone, 0.3242 g. or 0.001 mole, in 100 cc. of benzene and diethylaniline, respectively. Using the procedure described above it was found possible to get a positive test with 1 cc. of a 0.000025 molar solution of the ketone in benzene and a weaker test with 1 cc. of a 0.000025 solution of the ketone in diethylaniline.

Phosgene.—The concentration of phosgene in the stock benzene solution was determined by the method of Kling and Schmutz,[6] and this solution was progressively diluted with benzene until no positive color test was obtained. In carrying out the several tests, 1 cc. of the phosgene solution and 1 cc. of the dialkylaniline were placed in a test-tube, thoroughly shaken and then 1 cc. of a 2.25 molar solution of phenylmagnesium bromide solution was added and the resulting mixture again shaken for a moment at room temperature. When the mixture was directly hydrolyzed with water, it was possible to get a color test with a solution containing 0.0259 g. of phosgene per cc. of benzene. The delicacy of the test was not improved by allowing sealed tubes to stand for *sixty* hours prior to the addition of the Grignard reagent. By heating for one hour in a sealed tube[7] at 118° it was possible to detect a concentration of 0.00129 g. of phosgene in 1 cc. of benzene. The same delicacy was noted when anhydrous aluminum chloride was added to the phosgene in the amine and benzene solution.[8]

With diethylaniline in place of dimethylaniline, a test was obtained with 0.0259 g. of phosgene per cc., with practically no time on standing. When heated for one hour in a sealed tube at 118°, a positive test was obtained with 0.0129 g. per cc.

With di-n-propylaniline a test was obtained with 0.0129 g. per cc. directly after mixing the solutions at room temperature.

With di-n-butylaniline a test was obtained with 0.0259 g. per cc., also directly after mixing the solutions at room temperature.

Effect of Different Grignard Reagents.—In order to ascertain whether the delicacy of the test could be enhanced by the use of a particular organomagnesium halide, the following results were obtained with several typical Grignard reagents and the tetraethyldiaminobenzophenone. A poor color test was obtained with a 0.001 molar solution of the ketone and 2 molar ethylmagnesium chloride, and negative tests were obtained with the same concentration of ketone and 3 molar n-butylmagnesium bromide and 2 molar benzylmagnesium chloride, respectively. Phenylmagnesium bromide of 0.35 molar concentration gave a weak test with 0.001 molar ketone, and an excellent test

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[5] The authors wish to thank Dr. E. K. Bolton and Mr. F. B. Holmes for this ketone.

[6] Kling and Schmutz, Comfit. *rend.*, 168, 773 (1919). See, also, Scholvien, *Ber. pharm. Ges.*, 3,213 (1893).

[7] In these cases the Grignard reagent was only added after the phosgene and amine were heated.

[8] Aluminum chloride reacts with phenylmagnesium bromide. Apparently the sensitivity of this test was not increased by allowing the mixture to stand in a sealed tube for one hour prior to the addition of phenylmagnesium bromide.

with 0.01 molar ketone.[9] In general, a concentrated solution (2.25 molar and upwards) of phenylmagnesium bromide appears to be best suited for the tests described in this paper.

Summary

The sensitive color test for reactive organometallic compounds can be used as a delicate test for Michler's and related ketones. It is less satisfactory for phosgene and dialkyl anilines.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY!

THE CHEMISTRY OF THE LIPOIDS OF TUBERCLE BACILLI. XIV. THE OCCURRENCE OF INOSITE IN THE PHOSPHATIDE FROM HUMAN TUBERCLE BACILLI[1]

BY R. J. ANDERSON

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Introduction

The phosphatide fraction, A-3, isolated from the human type of tubercle bacilli, strain H-37, after it had been hydrolyzed with dilute sulfuric acid, was found to yield about 67% of fatty acids and about 33% of water-soluble material.[2] On concentrating the aqueous solution, a thick sirup was obtained from which we isolated glycerophosphoric acid, a small quantity of a colorless crystalline substance, crude mannose phenylhydrazone[3] and finally obtained a good yield of glucosazone.

We have recently examined the crystalline substance which separated from the concentrated sirup and it has been identified as ordinary inactive inosite. That inosite should be present in tubercle bacilli is not surprising, since it appears to be universally distributed in all living cells, but the occurrence of inosite in an ether-soluble lipoid was unexpected. The nature of the inosite linkage in the phosphatide molecule is still unknown, but it must have been combined in some manner either with the carbohydrate complex or with fatty acids.

Experimental Part

The inosite crystals had been obtained in the following manner. After the phosphatide, A-3, had been hydrolyzed by boiling with dilute sulfuric acid, the fatty acids

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[9] This is in agreement with earlier work by Gilman and Heck (see Ref. 1b of this paper), who showed that the color was more pronounced with more concentrated solutions of Michler's ketone.

[1] The present report is a part of a cooperative investigation on tuberculosis; it has been supported partly by funds provided by the Research Committee of the National Tuberculosis Association.

[2] Anderson, *J. Biol. Chem.*, 74, 537 (1927).

[3] Anderson and Renfrew, THIS JOURNAL, 52, 1252 (1930).

were removed by extraction with ether and the aqueous solution was freed of sulfuric and phosphoric acids by adding a slight excess of barium hydroxide. After the solution had been filtered, the excess of barium was removed quantitatively with sulfuric acid and the filtered solution was concentrated under reduced pressure to a thick sirup. The sirup was extracted with alcohol in order to remove the glycerophosphoric acid and on neutralizing the alcoholic extract with barium hydroxide, the barium glycerophosphate separated as a white amorphous precipitate which was filtered off. The filtrate was concentrated to dryness, the residue was dissolved in water and the excess of barium was removed quantitatively with sulfuric acid. The barium sulfate was filtered off and the filtrate was concentrated and combined with the main portion of the sirup which was insoluble in alcohol. The sirup was then concentrated in a vacuum desiccator, when crystals formed; these were isolated by washing off the adhering sirup with cold dilute alcohol. The crude crystals after combining the material from several hydrolyses weighed about 0.7 g. On combustion a small amount of ash was left which apparently consisted of magnesium carbonate.

For purification the substance was twice recrystallized by dissolving it in a little hot dilute acetic acid and adding alcohol until crystals began to form in the hot solution. On standing for a few hours or overnight at room temperature, the substance separated almost completely. It was recrystallized twice in the same manner from hot water by adding alcohol. The purified crystals weighed 0.55 g. and were practically free from ash. Large, colorless prismatic crystals were obtained which did not contain any water of crystallization.

The substance gave the Scherer reaction and when heated in a capillary tube it melted at 224–225°. There was no depression of the melting point when the substance was mixed with some purified inactive inosite, prepared from phytin, which melted at 224–225°.

For analysis the powdered crystals were dried at 61° in vacuo over dehydrite but there was no loss in weight.

Anal. Subs., 0.1387: CO_2, 0.2033; H_2O, 0.0860. Calcd. for $C_6H_{12}O_6$ (180): C, 40.00; H, 6.66. Found: C, 39.97; H, 6.93.

Summary

One of the water-soluble cleavage products of the phosphatide obtained from the human type of tubercle bacilli has been identified as inactive inosite.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE UNIVERSITY OF BRUSSELS]

THE ACTION OF OXYGEN ON 1,4-DIMETHYLCYCLOHEXANE[1]

BY G. CHAVANNE[2] AND MLLE. E. BODE[3]

RECEIVED DECEMBER 4, 1929 PUBLISHED APRIL 7, 1930

In a note presented to the Bulletin of the Science Section of the Belgian Academy in February, 1926, one of us gave an account of qualitative observations made on the change which samples of dimethylcyclohexanes had undergone when kept in contact with the air for several years. We also made preliminary- observations on the spontaneous oxidation of 1,3-dimethylcyclopentane. The latter phenomenon occurs at ordinary temperatures sufficiently rapidly to have been studied more closely and is described in a note appearing in the *Bulletin de la Société Chimique de Belgique.*[4]

Since then, thanks to grants from the American Petroleum Institute, we have been able to go more deeply into this study of the oxidation of different cyclohexane and cyclopentane hydrocarbons with side chains. This paper contains the observations made on one of them.

The 1,4-dimethylcyclohexane was prepared by the hydrogenation of very pure p-xylene (m. p. 13.10"). The saturated cyclic hydrocarbon so obtained is not a definite chemical individual, but a mixture of two stereoisomers, the relative proportions of which vary with the conditions of hydrogenation. The use of nickel catalysts at temperatures between 160 and 180" gave a product which distilled almost completely at 121.0–121.5° under a pressure of 750.6 mm. It is defined by d_4^0 0.7872, d_4^{15} 0.7746, and by a critical solution temperature in aniline of 50°. When platinum black at ordinary temperature is used as a catalyst, in an acetic acid medium, we obtain a saturated hydrocarbon distilling almost completely from 121.75 to 122.25° under a pressure of 733.8 mm. It is defined by d_4^0 0.7930, d_4^{15} 0.7804, and by a critical solution temperature in aniline of 48.5". These constants are for products perfectly purified from all trace of residual xylene.

Spontaneous Oxidation at Room Temperature and in Diffused Light.—AQO-cc. sample of the hydrocarbon was enclosed in a cylindrical glass reservoir of 420-cc. capacity, which was connected with a mercury manometer and which communicated by means of tubes to stopcocks leading, respectively, to an exhaust pump and to a gasometer filled with oxygen. After chilling the reservoir in ice, it was exhausted and oxygen then allowed to enter, passing over dehydrating substances. The stopcocks are then separated by sealing off the tubes leading to them, and the apparatus is put in a place where it will

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[1] This paper contains some of the results obtained in an investigation on "Action of Oxygen and Air on Cyclopentane and Cyclohexane Hydrocarbons with Side Chains," listed as Project No. 2 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 No. 2.

[3] American Petroleum Institute Research Assistant.

[4] *Bull. soc. chim.* Belg., 36,206 (1927).

not receive the direct rays of the sun. A movable cathetometer on a shaft graduated in millimeters with a vernier for tenths enables the operator to read the level of the manometer. Before each reading the reservoir is surrounded with ice. We are thus enabled to follow the diminution of the interior pressure as a function of time. The numerical results below show the absorption of oxygen by the hydrocarbon.

Sample	Date of reading	Pressure, mm. Hg	Press. decrease
Prepared from Ni	13–12–1926	666.3	..
	26– 9–1927	651.2	15 1
	9– 6–1928	636.6	29.7
Prepared from Pt	20–12–1926	666.8	..
	26– 9–1927	655.9	10.9
	9– 6–1928	648.8	18.0

The real values of the diminution of pressure of the oxygen are doubtless greater than the measured decrease, for the oxidation reaction actually produces other gases, as we shall see later.

The spontaneous oxidation of the hydrocarbon in diffused light thus shown is much less rapid than that observed by one of us under the same conditions with dimethyl-1,3-cyclopentane.[4] In the latter case we found a diminution in pressure of 528.5 mm. in 151 days.

The difference in the vapor pressures of the hydrocarbons at room temperature is inadequate, by far, to account for the enormous inequality of the velocities of autoxidation. Some constitutive influence is surely dominant.

After opening the apparatus, we detected peroxides in the liquid by employing potassium iodide and indigo carmine as reagents.

Spontaneous Oxidation at Room Temperature and in Sunlight.—Ten cc. of each sample was enclosed, with a known pressure of oxygen, in a larger flask of about two liters' capacity and having a narrow neck which was further reduced in dimensions by drawing down to a convenient size. To the bottom of each flask there was sealed a cylindrical vessel of about 20-cc. capacity. To the neck of the flask a narrow side tube was sealed, drawn down to capillary size and sealed off at its end. After placing the hydrocarbon in the cylindrical vessel, the system is cooled in ice, evacuated and then filled with dry oxygen at a known pressure, which is indicated by a manometer. Then the vessel is sealed at the neck. The flask is then inclined in such a manner that the hydrocarbon contained in the small vessel spreads over its surface, and presents a large surface to the oxygen. When the exposure is deemed sufficient, the flask is straightened again, frozen under the same conditions as before, and the capillary tip of the tube sealed on at the side of the neck is broken off inside a thick-walled rubber tube. This tube connects the capillary to a manometer without adding appreciably to the total volume.

After 138 days of exposure on the roof of the University (from May 12, 1927 to September 27, 1927), we found a diminution of pressure of 61 mm. for the sample prepared from nickel, and 83 mm. for the other. These values correspond, respectively, to the absorption of 160 and 220 cc. of oxygen at 20° and 760 mm. These are, for the reasons indicated above, minimum values. The autoxidation is much more rapid here than it was in the experiments made in diffused light. The oxidized liquids give tests for peroxides, but do not contain hydrogen peroxide, for Crismer's reagent (citric acid–ammonium molybdate) gives negative results.

The peroxide is destroyed when the excess of hydrocarbon is distilled under atmospheric pressure, but if we carry out the distillation at 20-mm. pressure, warming the system to 40° and condensing the vapor at −78°, we obtain a residue which gives exclusively the reactions of a peroxide, to a high degree. This residue also contains other oxidized compounds. In fact, the titration of peroxides in a known weight of residue, employing an iodide solution acidified by acetic acid, leads to values of oxygen combined as peroxide which are much smaller than the amount of oxygen which disappeared, assuming that the peroxide acts on an acceptor by only one atom of active oxygen. In the case of the nickel sample about one-fifth of the oxygen that disappeared was found combined as peroxide.

Influence of Temperature on the Oxidation. Experiments in Diffused Light at **100°.**—These experiments were carried out with considerably greater hydrocarbon masses, which required large volumes of oxygen. The apparatus consists of flasks of 2 or 3 liters' capacity, connected by their narrow necks to a vertical glass cylinder, 40 cm. long and 5 cm. in diameter, which acts as an air condenser. Its upper part, drawn out, carries a side tube which is closed by a stopcock near its free end, the stopcock being first tested for leaks. From this side tube a manometer tube leads to the mercury reservoir. After introduction of the hydrocarbon, the apparatus is sealed, evacuated after chilling and filled with oxygen in such a manner that the pressure inside will not exceed that of the atmosphere when the required temperature is reached. The volume of oxygen introduced is read on the gasometer. Measured quantities are later led in from time to time, depending on the pressure given by the manometer. On certain occasions, particularly when the speed of absorption has slackened sufficiently, the residual gases may be evacuated by a mercury pump, in order to refill the system with fresh oxygen, and to carry out analyses. The lower part of the flask is placed in an air-bath which reaches to the level of the free hydrocarbon surface. This air-bath is kept at the required temperature by an electric hot-plate. The temperature is given by a thermometer whose bulb is placed in the air-bath, where it touches the wall of the flask. It is kept between 100 and 110°.

When the gas is pumped out, the hydrocarbon liquid is previously cooled in a freezing mixture of ice and salt, and the evacuated gas, before it can reach the pump, passes through a tube cooled to −78° by carbon dioxide snow and acetone, which traps the entrained hydrocarbon vapor.

We give as an example the following table, which shows the progress of the absorption of oxygen by a sample of 50 cc. of hydrocarbon (38.7 g.), prepared by hydrogenation over nickel.

Date of introduction of oxygen	Time	Liters of oxygen introduced, corrected to N. T. P.
19–12–1927	1st day	1.465
30–12–1927	12th	0.590
6–1–1928	19th	.895
12–1–1928	25th	1.220
14–1–1928	27th	1.280
16–1–1928	29th	1.190
19–1–1928	32nd	1.090
27–1–1928	40th	0.790
10–2–1928	54th	.500
	Total.	9.020

With a freshly distilled hydrocarbon, the absorption of oxygen accelerates after a slow start, then it becomes slower and slower, and finally reaches a state where the manometer shows—not diminution—but an increase in pressure. There are gaseous products formed by the oxidation, and the volume of these produced in unit time may possibly exceed the volume of oxygen absorbed.

Analysis of the Gas Phase.—The analysis of gas (1345 cc.) collected at the end of the experiment cited above showed that it contained much carbon dioxide (840 cc.) but very little oxygen (35 cc.—about 0.5% of the oxygen introduced into the apparatus). Saturated cyclic hydrocarbons act as an excellent absorbent for oxygen at *100°*.

In the gas residue left after treatment with alkaline pyrogallol ammoniacal cuprous chloride indicated the presence of a little carbon monoxide. Agitation with fuming sulfuric acid gave no further diminution of volume, but the gas still contained combustible components. Rough eudiometric analysis showed that the ratio of volume diminution by explosion to the subsequent diminution of potash corresponded to a mixture intermediate to methane and ethane. The gaseous residue is nitrogen which accompanied the oxygen used.

Carbon monoxide, present in gas mixtures at low concentrations, is probably incompletely removed by cuprous salts. Furthermore, the eudiometric analysis of the combustible gases remaining after such absorption was incapable of furnishing an accurate indication of their nature. To identify and analyze them really requires fractional combustion by copper oxide.

We obtained the necessary gas mixture by treating 30 g. of hydrocarbon, kept for many months in a partly filled flask with oxygen at 100" in an apparatus with a total capacity of 2700 cc. We show below the progress of oxygen absorption compared with that observed in the previous experiment. It shows the favorable influence on the speed of oxidation at 100° of the slight previous alteration of the hydrocarbon employed.

	Volumes of oxygen introduced corrected to N. T. P., cc.
1st day	1870
5th day	1370
7th day	1350
10th day	1140
13th day	1365
	Total, 7095

On the seventeenth day 480 of the 1200 cc. of gas present was pumped through a tube at −78° and extracted for gas analysis. This showed 37.8% of carbon dioxide and 19.2% of oxygen. After absorption of these two, the residual gas formed 43% of the initial amount.

Two hundred cc. of this residue was separated into two fractions by passing the sample slowly through a Moissan tube cooled to −183° in order to condense the homologs of methane; 90 cc. remained in the vapor phase.[5] The part remaining in the tube is recovered separately by warming and pumping. This second fraction had a volume of 110 cc. Each of these fractions was submitted to fractional combustion over copper oxide in a nitrogen atmosphere. It is known that hydrogen and carbon monoxide burn alone and completely at 275° under these conditions, and that it is necessary to work at 800" to obtain a complete and rapid combustion of methane and its gaseous homologs.

In this way we found for the uncondensed fraction: H_2, 18.4%; CO, 8.2% and CH_4, 2.85% (no volume variation by oxidation at 800°). For the second fraction the combustion at 275° showed H_2, 15.7%, and CO, 7.8%. The subsequent combustion at 800° gives an increase of 5.94% of the initial volume submitted to analysis and the

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[5] Analysis carried out by Mr. O. Miller. The results obtained in analyzing gases resulting from the oxidation of various cyclic hydrocarbons in this manner will soon be collected in a paper.

contraction produced by the potassium hydroxide is 14.6% So there must be at least one saturated gaseous homolog of methane present.

This may be ethane, but is not pure propane. The second hypothesis would lead to the fallowing percentages in the second fraction: CH_4, 5.7, and C_3H_8, 2.97. It would follow that methane is liquefied in the cooled tube until its partial pressure, corresponding to 2.85%, is 22 mm. According to the measurements of Karwat[6] on the vapor pressure of methane, this would indicate that the temperature of the tube was −191.5°. This is the boiling point of an equimolecular mixture of oxygen and nitrogen. But our liquid refrigerant was liquid industrial oxygen, with a very low nitrogen content. (It yields a gas containing 4.5% of nitrogen.) We are able to conclude, on the other hand, that ethane is present. The respective percentages would be: CH_4, 2.72, and C_2H_6, 5.94. Comparison of this value for methane with that observed in the uncondensed fraction indicates, then, that there was no liquefaction of this gas, and the results of analysis of the condensed fraction, recalculated on the assumption that the gas is freed of ethane by liquefaction, are in fairly good agreement with the results found for the gaseous fraction. Calcd.: H_2, 16.7; CO, 8.3; CH_4, 2.90. Found: H_2, 18.4; CO, 8.2; CH_4, 2.85. All these calculations give the gas obtained after oxidation the following percentage composition: CO_2, 37.8; N_2, 29.7 (by difference); O_2, 19.2; H_2, 7.3; CO, 3.4; C_2H_6, 1.4; CH_4, 1.2

Its volume at the time oxidation was stopped, computed by calibration of the apparatus and changed to standard conditions of pressure and temperature, was 1200 cc.

From this we deduce that, of the 7095 cc. of "oxygen" introduced, 355 cc. was nitrogen, leaving 6740 cc. of pure oxygen: 230 cc. was recovered, so 6510 must have been used up. About 455 cc. of carbon dioxide and 40 cc. of monoxide were formed at the expense of 475 cc. of oxygen. This means that about 6 liters took part in the formation of solid and liquid oxidation products. Simultaneously, about 90 cc. of hydrogen, 15 cc. of methane and 17 cc. of ethane were formed.

This experiment also enabled us to establish the formation of water during oxidation of the hydrocarbon. The liquid oxidation products were gently distilled under atmospheric pressure, and first began to pass over at 85°. At first a heterogeneous mixture was collected, but the distillate soon became homogeneous. We collected everything which distilled up to 102–103° and separated the two layers which had formed. The lower layer is composed mainly of water, freezing slightly below 0°; the upper layer consists wholly of hydrocarbons which have escaped oxidation and have been carried over by the water. We found about 1.10 g. of water.

Study of the Solid and Liquid Phases of the Oxidized System.—For this work we used the product obtained from 100 cc. or 77.5 g. of hydrocarbon prepared from nickel which, after absorption of 14.680 liters of pure oxygen, weighed 92.2 g., and the product obtained from 50 cc. or 39 g. of hydrocarbon prepared from platinum which, after absorption of 6.870 liters of oxygen, weighed 46.5 g. We thus had a total of 138.7 g. of oxidation product with which to work. It was a clear yellow liquid, more viscous than the hydrocarbon, and contained white crystals. Preliminary observations having revealed that these crystals are only slightly soluble in cold ether, while the liquid is completely miscible with this solvent, we rinsed out the flasks with ether, separated the crystals by filtration, and washed them with a little cold ether. They weighed 3.2 g. The ethereal solution is acid. It is agitated with a slight excess of potassium carbonate solution to dissolve the acid products. This solution is decanted, the alkaline liquid L_A is agitated with fresh ether to dissolve as much of the neutral products which it contains as possible, and this ether is added to the preceding ethereal solution, L_N.

Alkaline Solution—L_A.—It is gradually acidified with normal sulfuric acid in the

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[6] Karwat, *Z. physik. Chem.*, 112,488 (1924).

presence of methyl orange. During the addition of the acid it becomes turbid and gives off the odor of fatty acids. It is extracted several times with ether, and the resulting ethereal solution L_A^2 is rapidly dried by agitation with calcium chloride. The aqueous solution L_A^1 is distilled.

Solution L_A^1.—The water which distils over contains ***acetic acid*** (**0.062** g. mole). It is distinguished after neutralization by precipitation and analysis of the silver salt. Calcd.: Ag, **64.7.** Found: Ag, **64.4, 64.6.**

The precipitation of silver salts is accompanied by reduction and the precipitate must be recrystallized twice in succession by cooling the boiling filtered solution. This reduction must be attributed to substances other than formic acid, in large part at any rate. The action of mercurous chloride on a neutralized sample of the liquid, taken before precipitation, gives doubtful results.

The residue from distillation is composed of crystals of potassium sulfate impregnated with an odorous oil, which was extracted with ether. After getting rid of the ether, we are left with about **2.5** g. of a slightly volatile product which distils under a pressure of **3** mm.

Between **130** and 150° we obtain a viscous acidic liquid (H_1) (see below, ketonic acids), accompanied by neutral crystals melting between **145** and **155"** (H_2). These products will be met again and will be studied later.

L_A^2 **Ethereal** Solutions of Easily Extractible Acids.—The ether is separated by means of a fractional distillation column, and the residue is first distilled under atmospheric pressure up to **153".** Between **70** and 120° there distil a few drops of a liquid with a sharp odor, which reacts as an aldehyde in the presence of decolorized fuchsine, but contains no formic acid. Between **120** and **153"** a liquid distils (**1.25** g.), which requires **0.011** g. mole of sodium hydroxide for neutralization.

After neutralization, ether extraction leaves some insoluble droplets of an odorous neutral liquid, while the alkaline salt remaining in solution is changed to the silver compound. There is no reduction. Analysis gives Ag, **63.2, 63.5%.**

During the calcination we noticed a fatty acid odor. It is due to silver acetate (Ag, **64.7).** containing, no doubt, a small amount of the silver salt of a higher acid.

We continued the distillation under reduced pressure with these results:

I.	From **52** to 105°, and mainly from **100** to 105°	**23** mm.	**1** g.
II.	From **100** to 142°, and mainly from **109** to **120"**	**18** mm.	**1** g.
III.	From **126** to **149°**, and mainly from **140** to **149°**	**5** mm.	**3.6** g.
IV.	From **146** to 165°	5mm.	3.25 g.

The residue weighed about **1** g.

By employing the formation of the silver salts of I and II, we have detected the presence of a hexanoic acid. Calcd. for $C_6H_{12}O_2Ag$: Ag, **48.4.** Found: 48.2, 48.3, 48.5.

The remainder of each of these fractions was treated with thionyl chloride and the reaction product mixed with aniline to form the anilide of the acid. This anilide was purified by crystallization in light petroleum ether; the crystals obtained from I melted at 84.5°, those from II at **82.0°.** The quantity at our disposal did not permit recrystallization to the point where constant values would be obtained, but by testing a mixture consisting of the crystals melting at 84.5°, and those of the anilide of synthetic β-methylvaleric acid (m. p. **86.6°**), their identity was revealed, for the mixture melted at almost exactly **86°**, when the two components were present in equal amounts.

This shows that one of the products of the oxidation of the hydrocarbon is

$$CH_3CH_2CH(CH_3)CH_2COOH$$

The greater part of Fraction III (**3.1g**), was neutralized by a **1** *N* solution of potassium hydroxide, **19.35** cc. of the latter was required, which gives a molecular weight of

160. It is a maximum value of the equivalent weight of an acid contained in this fraction. The neutralized solution is extracted with ether to eliminate as much of the neutral impurities as possible, then reacidified with sulfuric acid, and again extracted many times with ether. After drying the ethereal solution over calcium chloride, the ether is expelled and the residue distilled under reduced pressure. At a temperature of 167–170° and under a pressure of 13.5 mm., 2.3 g. was collected. The molecular weight determined by titrating 0.4435 g. with 0.1 N potassium hydroxide (27 9 cc.) was 159. This acid is water soluble.

It is a ketonic acid. It gives a semicarbazone which shows an instantaneous (30 sec.) melting point of 153°, when purified by crystallization in methyl alcohol. This semicarbazone has acid properties. Its molecular weight, found by the neutralization of 0.3054 g. with 14.25 cc. of 0.1 N potassium hydroxide, is 214.

This ketonic acid contains the acetyl group. Iodine in alkaline solution gives the iodoform test. Therefore it may be represented by $CH_3COC_5H_{10}COOH$ (mol. wt., 158). We have established the constitution of this acid by synthesizing it from 1,4-dimethylcyclohexene-1. This unsaturated hydrocarbon, which is prepared by making use of the catalytic dehydrating action of *p*-toluenesulfonic acid on 1,4-dimethylcyclohexanol-1, boils at 127.6–128.1° under 753.4-mm. pressure. Its density is d_4^{15} 0.8051.[7]

Twenty-two grams of this hydrocarbon was oxidized by the theoretical amount of a 2% solution of potassium permanganate, the first part of the latter being added during one day at a temperature near 0". The rest was mixed in at room temperature. The colorless liquid obtained was siphoned from the dioxide sediment, the latter washed by decantation and finally separated by filtration.

The mixture of alkaline liquids was concentrated to a volume of 400 cc. on a water-bath in a current of carbon dioxide; after extraction with ether to remove as much of the neutral products as possible, the liquid was freely acidulated with sulfuric acid, saturated with ammonium sulfate and finally was extracted with ether several times. After drying the ethereal solution over calcium chloride, the ether was evaporated and the residue distilled under reduced pressure. Under 12-mm. pressure, 0.7 g. was collected up to 85°, and under 5 mm., 5.75 g. up to 175".

This last fraction is formed of a mixture of liquid and crystals, petroleum ether dissolving the latter without mixing with the liquid. The crystals can therefore be extracted with petroleum ether; the dense layer of the initial liquid, separated by decantation, is warmed to rid it of dissolved petroleum ether, placed in a water-alcohol solution, and treated with semicarbazide hydrochloride and sodium acetate. The precipitate of semicarbazone is separated, washed with ice water, and purified by crystallization in methyl alcohol.

The point of instantaneous fusion (30 sec.) of the crystals is 152 5°. The mixture of these crystals with those of the semicarbazone of the ketonic acid obtained by oxidation, melt at the same point. The two ketonic acids are identical. Thus the oxidation of 1,4-dimethylcyclohexane by oxygen gives the β-methyl-δ-acetylvaleric acid

$$CH_3COCH_2CH_2CH(CH_3)CH_2COOH$$

This ketonic acid, which is not described in the literature so far as we know, was prepared in the pure form by the hydrolysis of the semicarbazone by hydrochloric acid. It boils at 141.2" under 2.5-mm. pressure.

From Fraction IV of the distillate of acids obtained under reduced pressure, we isolated 2.5 g. of the same acid ketone; b. p. 137.8–141.2" under 2-mm. pressure; mol.

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[7] Sabatier gives b. p. 125° under 760 mm., d_4^0 0.8207, d_4^{14} 0.8111; *Compt. rend.*, **141,** 21 (1905); 142, 438 (1906); *Ann.*, [8] **10,** 558 (1907). Zelinsky gives b. p. 128 5°; d_4^{20} 0.8005; *Ber.*, 41,2632 (1908).

wt., 156; semicarbazone, m. p. 152.5'. Neither in this fraction nor in the residue has any other acid been identified.

The viscous acid liquid H, obtained above in the distillation residues of the aqueous acid solution L^1_A, a liquid which distils between 130 and 150° (3 mm.), is formed largely of **β-methyl-δ-acetylvaleric** acid.

L_N Ethereal Solution of Neutral Products.—This solution is dried over sodium sulfate, and the ether is expelled on the water-bath. The distilled ether is then gently rectified with a large Crismer column. This leaves a residue which is then fractionated. Under normal pressure, we obtain 8 g. of a water-insoluble liquid between 120 and 123°, its density being d^{15}_4 0.7734. This is the non-oxidized hydrocarbon. There remains a slight residue of long needle-like crystals, melting near 50° (see below, **1,4-dimethylcyclohexanol-1**).

After evaporating the greater part of the ether from L_N on the water-bath, the distillation is continued with a paraffin-bath at atmospheric pressure, the temperature being gradually raised to 165–170°. Up to 94° we obtained 7.5 g. of a liquid composed almost entirely of ether. From 94 to 123°, 9.5 g. of a heterogeneous liquid came over. It contained an aqueous layer weighing 1 g., and a layer of lower density.

The aqueous layer contained formic acid, as was clearly shown by the reduction of mercuric chloride in the presence of formate-free sodium acetate. The upper layer (8.5 g.) consists principally of regenerated hydrocarbons, but it contains—like the aqueous layer—an aldehyde, which is shown by its action on Schiff's reagent. It was not possible for us to determine the nature of this aldehyde, due to its low concentration.

The distillation is then carried further under reduced pressure, the flask acting as receiver, being followed by a Moissan tube immersed in a freezing mixture. Commencing at 40 mm., the pressure was gradually reduced as the boiling point rose. The results were: I, in the Moissan tube, we obtained 3.4 g. of a heterogeneous liquid mixture; II, from 70° and 40 mm., to 85.5° and 31 mm., 22.7 g. of a substance which was solid at room temperature; III, from 85.5" and 31 mm. to 92° and 18 mm., 20.1 g. of a solid (at room temperature); IV, from 92 to 98° and 18 mm., 3.6 g. of a liquid containing some suspended crystals. The distillation stopped here sharply, and did not resume until the temperature had reached 120°, under 2-mm. pressure. Let us first consider the neutral volatile products distilling below 98° (18 mm.).

In the heterogeneous fraction, I, we found about 2 g. of the original hydrocarbon forming the greater part of the upper layer. The lower layer is an aqueous solution. Each contains a ketone which gives an instantaneous precipitate of a very insoluble semicarbazone when treated with semicarbazide hydrochloride and sodium acetate. This same ketone was found in the other three fractions.

Fractions II and III are dissolved in ether, and the solution is shaken with a concentrated solution of sodium bisulfite. A crystalline precipitate is formed and is collected and washed with ether. With this solvent (ether), the aqueous bisulfite layer is extracted, and these ether washings are added to the main ethereal solution. The precipitate and the bisulfite waters are separately distilled with a 2 N solution of potassium carbonate.

In both cases the first runnings give a heterogeneous mixture of water and ketone; later we get nothing but an aqueous solution. The successive fractions give immediate precipitates with semicarbazide. The distillation is continued as long as an appreciable precipitate is formed. The semicarbazone is separated, dried, washed in cold water and then recrystallized in a large excess of boiling water. After being desiccated, it shows a constant decomposition point of 243' (twenty sec.). The rapidity of precipitation of this semicarbazone, its insolubility in cold water, and its very slight solubility in boiling water, the ease of distillation with steam exhibited by the corresponding ketone, its distinctive solubility in water—all these properties are characteristic of acetonylacetone. But the decomposition point of the semicarbazone of the latter, according to the literature, is 223°. In order to check this value, the substance was prepared synthetically, beginning with ethyl acetoacetate and following the procedure of Knorr. Its semicarbazone has a decomposition point of 242°. The value given in the literature should be corrected. The mixture test indicated the identity of the two products. The oxidation of 1,4-dimethylcyclohexane at 100° yields acetonylacetone, $CH_3COCH_2CH_2COCH_3$. The quantity obtained, estimated by the weight of the semicarbazone, is of the order of half a gram.

The con-ketonic part of fractions II and III is in solution in ether. After drying this solution over potassium carbonate, it is distilled under atmospheric pressure until the ether has gone, and then low pressures are used. In this way the small interval between 83.4" under 45.5 mm. and 79.2" under 43.5 mm. yields an important fraction weighing 25 g. It solidifies completely in the receiver. In a Moissan tube, immersed in a freezing mixture and connected to the receiver, 3 g. of a liquid is collected simultaneously. A distillation residue of 4 g. remains. The rectification of the first fraction collected in the freezing mixture and the tailings under atmospheric pressure gives on the one hand 2.5 g. of the original hydrocarbon and, on the other, 2.6 g. of the preceding solid. We thus obtain a total of 21 g. of the hydrocarbon submitted to oxidation, out of 116 g. put into the experiment.

The solid collected is distilled under atmospheric pressure. It distils from 170 to 172° under 760 mm. (corrected), and melts between 51.7 and 53°. It has an appreciable vapor pressure at ordinary temperatures and evaporates readily in the air. It is easily carried over by ether vapor. When sublimed it forms needles several centimeters long. It has a camphor-like odor.

Anal. Subs., 0.1301: H_2O, 0.1473; CO_2, 0.3571. Calcd. for $C_8H_{16}O$: C, 75.00; H, 12.5. Found: C, 74.92; H, 12.58.

It reacts as an alcohol. Its allophanate, when recrystallized from methyl alcohol, melts at 163° (in twenty seconds). This carbinol has been identified with 1,4-dimethylcyclohexanol-1.

Sabatier and Mailhe,[8] who prepared this compound, give its melting point as 50°, and its boiling point under 760 mm. as 170°. We have prepared it by synthesis from methylmagnesium iodide and *p*-methylcyclohexanone. The product melts at 52.8" and boils at 168.2–168.8° under 730-mm. pressure. The mixture of this synthetic compound and the carbinol obtained by oxidation melts between 51.7 and 53°. These two substances are easily dehydrated by warming with a trace of p-toluenesulfonic acid, each giving the same olefin with a boiling point between 127.6 and 128.1° under 753.4-mm. pressure.

The action of oxygen at 100° on 1,4-dimethylcyclohexane yields, therefore, an important quantity of 1,4-dimethylcyclohexanol-1. The latter is by far the preponderating oxidation product. Furthermore, it has been detected in the hydrocarbon oxidized at ordinary temperatures. The part of the hydrocarbon molecule sensitive to oxidation is thus the tertiary group, —CH<.

Fraction IV from the distillation of the neutral volatile products contains a little β-methylvaleric acid which has escaped from the carbonate extraction, a little acetylacetone, some crystals with a melting point of 193" identical with those separated by filtration of the crude product of oxidation, and 0.3 g. of a neutral non-carbonyl liquid with a camphor-like odor, which passed over at 180–187° under normal pressure. It has not been identified.

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[8] Sabatier and Mailhe, *Compt. rend.*, **141,** 21 (1905); *Ann. chim. phys.*, [8] **10,** 558 (1907).

Neutral Products of Low Volatility.—After distilling Fraction IV, a yellowish-brown sirup is left behind. It forms a homogeneous solution when treated with a mixture of ether and petroleum ether. 'Crystals soon begin to deposit from it. The crystallization is continued at 0° with frequent shaking and the crystals are separated by filtration and washed with a little cold ether. Two g, was collected in this way. These crystals are not pure—as their melting point ranges from **143** to 156°. **It** is the same crystalline mixture which we found above in the residue left by the distillation of the volatile acids. These solid substances were dissolved by the potassium carbonate solution during the extraction of the acids. They are neutral, but soluble in water.

After driving offthe solvents, ether and petroleum ether, by distillation, the residue is extracted with hot water. The aqueous solution is separated and evaporated on the water-bath. A residue is left which crystallizes in the desiccator (about **0.5** g.). After drying on a porous plate and washing with a little cold ether (about **0.5** g.), it still melts over the interval 143–155°. They are united with the preceding ones. Fractionation of the neutral liquid is then carried out by successive extraction with a **2** N potassium carbonate solution, then by entrainment in steam, and finally by distillation under 4-mm. pressure until the temperature has reached 200°. **A** very viscous deep brown residue remains.

The fraction extracted by the carbonate **(3** g.) distils between **107.5"** under **11 mm.** and **150"** under **2** mm. The fraction carried over by steam **(2.3** g.) distils between **120** and **150"** under 15-mm. pressure. The fraction distilling under **4 mm. (5.5** g.) is rectified. **It** distils regularly between **135" (12.5** mm.) and **196" (2 mm.).**

No definite product could be isolated and identified in these fractions. Substances with the properties of esters occur in the last two. The product of the saponification of the fraction carried over by steam contains a fatty acid salt with a caproic odor, and a neutral alcoholic product distilling between **130** and **133° (17–18 mm.)** which crystallizes partially at room temperature. Two analyses of this neutral product gave H, **11.24, 11.21; C,** 69.17, 69.43, without throwing any light on its constitution.

The saponification products of the rectified fractions of the liquid distilling under 4 mm. up to **200"** contain salts of ketonic acids, and the neutral alcoholic part also crystallizes partially at ordinary temperatures.

Neutral Crystalline Products.—We have on the one hand the crystalline component separated from the ether-treated oxidation product by filtration **(3.2** g.). This component, which is slightly soluble in ether, melts at **193±1°.** We have, on the other hand, crystals which can be extracted by water, and which are precipitated from the neutral, slightly volatile products by treatment with ether and petroleum ether at 0° **(2.5** g.). They melt at 143–156°.

The first were purified by solution in pure, dry, boiling acetone, and subsequent crystallization from the cooled, agitated solution.

The others are equally soluble in cold acetone, and crystallize incompletely on cooling, or by evaporation only, if the solution is dilute. Crystallization by cooling the concentrated solution gives pure crystals on rare occasions, and it is only by slow, patient evaporation of a dilute solution that separation of the original substance into two pure constituents can be completely effected. Since crystals formed in this manner are relatively large, they may be easily recognized as being of two types, which can be separated by hand picking. The monoclinic form melts at **193°±1.** They are identical with those obtained by filtration of the crude oxidation product, and are the less soluble. The others form tetragonal groups of four orthorhombic units, and melt at **165.5–166°.**[9] These two pure substances act in an analogous manner in the presence of

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[9] We are indebted to Mr. Gilta, Assistant Professor at the University of Brussels, for these crystallographic data.

solvents. Only slightly soluble in ether, they are more so in acetone and quite soluble in hot water; 100 g. of boiling water dissolves approximately 3.5 g. of the crystals which melt at 193°, and more than three times as much of the other variety. They sublime simultaneously under reduced pressure with a speed which is already appreciable at 100°.

The crystals melting at 193°, obtained by slow evaporation of the acetone solution, rapidly become opaque near 95°. It is a polymorphic transformation, and is not accompanied by any elimination of water or acetone of crystallization; then, as the temperature is increased, the crystals sublime, giving needles which radiate from a central point. The fusion point, which must be determined by heating rapidly enough to avoid complete vaporization, evidently depends on the amount of the latter form present.

The two substances are isomers with the molecular formula $C_8H_{16}O_2$. Their percentage composition has been determined by the method of Ter Meulen and Heslinga [10]

Anal. of the 193° variety. Subs. I (large crystals obtained by slow crystallization from acetone), 0.0594: H_2O, 0.5094; CO_2, 0.1448. Found: H, 11.18; C, 66.48. Subs. II (needles obtained by sublimation in a stream of nitrogen), 0.0525: H_2O, 0.0524; CO_2, 0.1288. Found: H, 11.09; C, 66.91.

Anal. of the 165.5–166° fraction. Subs. I, 0.0554: H_2O, 0.0547; CO_2, 0.1354. Found: H, 10.97; C, 66.65. Subs. II, 0.0628: H_2O, 0.0625; CO_2, 0.1533. Found: H, 11.13; C, 66.52. Calcd. for $C_8H_{16}O_2$: H, 11.18; C, 66.61.

The approximate molecular weight was determined by microebullioscopic methods in aqueous solution in a modified Cottrell apparatus which contained a micro Beckmann thermometer. The values obtained are not very precise, due to the slight solubility of the 193° compound, the smallness of the ebullioscopic constant of water, and the small amount of the substance at our disposal. However, these values seemed to us to be sufficient to establish the molecular formula of the two compounds as $C_8H_{16}O_2$.

193° Compound—0.1529 g. dissolved in 5.090 g. of water raised the boiling point 0.105°. Therefore, mol. wt. = 149.

165.5–166° Compound: I—0.251 g. dissolved in 5.040 g. of water raised the boiling point 0.19". II—0.443 g. dissolved in 5.04 g. of water raised the boiling point 0.275°. Therefore, from I: mol. wt. = 136 and from II—mol. wt. = 166. Calculated for $C_8H_{16}O_2$ = 144.

These two isomers are two glycols, $C_8H_{14}(OH)_2$. The solubility characteristics of these two compounds led to this conclusion. We first tried to verify it by employing Zerewitinoff's hydroxyl determination method, using iso-amyl ether as the solvent for methylmagnesium iodide, and working in an atmosphere of pure nitrogen. The more soluble compound (165.5–166°) reacts fairly rapidly on the Grignard reagent at ordinary temperatures, 0.0918 g. giving 28.3 cc. of methane (N. T. P.). The calculated value for $C_8H_{14}(OH)_2$ is 28.6 cc. This compound is thus a 1,4-dimethylcyclohexanediol. The less soluble compound (193°), reacts only to a negligible extent under similar conditions. Even on warming the system, only a small fraction of the required volume of methane is liberated in a day. This has not seemed to us sufficient to conclude that we were not dealing with a di-alcohol, for its insolubility in the iso-amyl ether will furnish an explanation, since finely powdered saccharose acts in the same way.

When the 193° compound is powdered and added to a concentrated solution of hydrochloric acid, it dissolves very rapidly at room temperature, although it does not dissolve at all in water under the same conditions. Then the solution becomes cloudy, and finally begins to deposit minute crystals which are only very slightly soluble in the excess of hydrochloric acid. They are easily separated by filtration and drying on a

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[10] "Nouvelles methodes d'analyse chimique organique," by H. Ter Meulen and J. Heslinga, translated from the Dutch by T. Kahan, Dunod, Paris, 1927.

porous plate. They are finally placed in a desiccator containing fused potash. These crystals, which have a camphor-like odor, are insoluble in water, but soluble in alcohol and ether. They melt between 46 and 49°, and have an appreciable vapor pressure at ordinary temperatures. They contain some chlorine, but the latter is not easily detectable in a dilute alkaline solution at room temperature; this crystalline compound, whose formation is so easy, is not an oxonium salt. On the contrary, it may be saponified by an alcoholic solution of potassium hydroxide or sodium methoxide; this reaction takes place little by little at room temperature, is fairly rapid at water-bath heat, and was employed by us for chlorine determination by weighing the silver chloride formed from the chlorides. Subs., 0.1151: AgCl, 0.1808. Calcd. for $C_8H_{14}Cl_2$: Cl, 39.18; for $C_8H_{14}ClOH$: Cl, 21.8. Found: Cl, 38.85. So we are dealing with a dichloro ester, and the compound $C_8H_{16}O_2$ which melts at 193° is thus a 1,4-dimethylchlohexanediol.

Concentrated hydrochloric acid affects the more fusible isomer, $C_8H_{16}O_2$, just as it does the one above. We prepared a small quantity of its dichloro ester by the action of 1 g. of concentrated hydrochloric acid on 0.118 g. of this glycol. The crystals so obtained melted at 38.6–39.3°. They are saponified by sodium hydroxide in alcoholic solution. A determination of chlorine in these crystals has been made by using this saponification and precipitating the chloride ions as silver chloride. Subs., 0.0579: AgCl, 0.0901. Found: Cl, 38.5.

What might the constitution of these two isomers be? A group of facts has led us to consider them as bitertiary glycols. These facts are: (1) the preponderating formation of tertiary alcohol in the oxidation of the hydrocarbon. This indicates that the group $—CH\langle$ is the particular center of attack on the molecule. All experiments which we have made on the oxidation of cyclopentane and side-branch cyclohexane hydrocarbons confirm this. (2) The formation of acetonylacetone during oxidation: this indicates attack of the oxygen on two $—CH\langle$ groups para to each other. (3) The almost instantaneous transformation of the two isomeric diols into their chlorine derivatives by the action of concentrated hydrochloric acid, is not compatible with the properties of primary or secondary alcohols, according to classical observations. (4) In the products obtained by applying Wagner's reaction to 1,4-dimethylcyclohexene-1, we have not found any trace of these two diols. They are not the 1,2-diols. This reaction of Wagner tells us at the same time that if the 1,2-glycols are formed during the oxidation of the hydrocarbon by oxygen, they have only a transitory existence.

General Conclusions.—We may finally sum up in general fashion the oxidation of 1,4-dimethylcyclohexane by oxygen at 100°.

Of 116 g. of hydrocarbon at the beginning, 21 g. was recovered unchanged, which means that 95 g. was oxidized by 21.5 liters of oxygen, or about 25 liters of oxygen per molecular weight. The sum of the weights of the hydrocarbon which was affected and the oxygen used up is $95 + 30.7 = 125.7$ g. Oxidized liquid and solid products made up $138.7 - 21 = 117.7$ g., while the weight of the carbon dioxide formed is 5.2 g. Since the weight of the other gases is negligible, the total is 123 g.

The oxidation product which is present in the greatest proportion has been identified as 1,4-dimethylcyclohexanol, which gave about 30 g. of the pure product. The quantity formed, however, is doubtless much larger.

In order of decreasing weight, neglecting the water, the products are: as acids—β-methyl-δ-acetylvaleric 8 to 9 g., acetic 4–5 g., methyl-2-valeric about 2–3 g.; as neutral products—the 1,4-diol (m. p. 193°) **3.5** g., a second 1,4-diol (m. p. 165.5°) 2.0 g., acetonylacetone about 0.5 *g.*

Consideration of the oxidation products which we have succeeded in identifying shows that we may represent the reaction as a progressive splitting up of the hydrocarbon molecule. In the first phase, a peroxide results from the addition of an oxygen molecule to one tertiary —CH< group of the hydrocarbon. Then the peroxide decomposes according to one of the following processes. (1) It acts as an oxidizing agent in losing an atom of oxygen, and changes to a tertiary alcohol. The acceptor may be either another hydrocarbon molecule or an oxidation product already formed. The latter is in particular the carbinol, acting through its free tertiary group to give a 1,4-diol. (2) It may join the second oxygen atom to a neighboring carbon atom, the splitting of the ring between the two oxygen-bearing carbons being the first step in the formation of the ketonic acid we have found. (3) To account for the formation of *P*-methylvaleric acid, we must also assume a possible opening of the ring by the ketonic split of the tertiary carbinol (or of a 1,2-diol, resulting from the preceding method of evolution between the carbon atoms 1 and 6).

Admitting the same sensitivity of the tertiary group to oxygen when it is in the products of ring-splitting, and a repetition of the aforementioned reactions, we may account for the formation of acetonyl acetone, ethane, methane and acetic acid.

The appearance of hydrogen during oxidation is more mysterious. The phenomena of photolysis and autoxidation have been thoroughly investigated for alcohols at ordinary temperatures, but they seem to produce hydrogen only in the presence of acceptors, such as ketones which are transformed into pinacones.[11] The existence of free hydrogen in these systems has not been observed, as far as we know. Alcohols are dehydrogenated by copper heated to a point below 200'. Can this phenomenon take place, with a very feeble velocity, below 100° and in the absence of catalysts?

A very recent note by Briner and Schnorf,[12] which we have seen during the writing of this paper, contains a result equally unexpected, a result which should be compared with ours. These authors have observed that the ozonization of ethylene in the presence of a trace of water

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[11] Ciamician and Silber, *Ber.*, 34, 1530 (1901); 36, 1575 (1903); W. D. Cohen, *Rec.* trav. *chim.*, 38, 27, 113 (1919); Böeseken, Cohen and Langedijk, *ibid.*, 44, 173 (1925).

[12] Briner and Schnorf, *Helv. Chim. Acta.*, *12*, 154 (1929).

gives the dioxymethyl peroxide of Wieland and Wingler,[13] and that the liberation of hydrogen by the ozonide, a reaction which they established in a manner to dispel any doubt, is related to the decomposition of this product. This suggests that the formation of hydrogen may well be connected with a rearrangement of the primary peroxide in our case. Experimental work in progress can at least limit the field of hypothesis in this connection.

Summary

The experiments reported in this paper have shown that 1,4-dimethylcyclohexane absorbs oxygen at room temperature in diffused light. This absorption is slower than that previously determined under the same conditions for 1,3-dimethylcyclopentane. It is accelerated by direct sunlight. At 100° it becomes rapid. If the hydrocarbon is very pure, there is an initial period during which the absorption is slow. This induction period is greatly shortened by the presence of hydrocarbon which has already been oxidized.

The saturated hydrocarbon acts as an excellent absorbent at 100° in weak light, being capable of extracting all but a few parts per thousand of any oxygen present. Among the oxidation products we have isolated the following gases: CO_2, CO, H_2, CH_4, C_2H_6. The liberation of hydrogen during the oxidation is particularly to be noticed.

In the liquid and solid phases we have identified, aside from water, (a) acid products—traces of formic acid, acetic acid, β-methylvaleric acid, and β-methyl-δ-acetylvaleric acid, $CH_3COCH_2CH_2CH(CH_3)CH_2COOH$, which is not described in the literature, and whose synthesis we have effected; (b) neutral products—1,4-dimethylcyclohexanol-1, the stereoisomeric 1,4 dimethylcyclohexandiols-1,4, which have not been described in the literature, and acetonylacetone (*sym.-diacetylethane*).

We have prepared and briefly described the stereoisomeric 1,4-dimethyl dichloro-1,4-cyclohexanes, obtained from the corresponding diols. The preponderating oxidation product is 1,4-dimethylcyclohexanol-1.

BRUSSELS, BELGIUM

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[13] Wieland and Wingler, Ann., 431, 301 (1923).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MIDDLEBURY COLLEGE]

SOME OBSERVATIONS ON BENZOYLFORMIC ACID

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Benzoylformic acid was purified by repeated crystallization from carbon tetrachloride. The pure acid (snow-white) was stored in the dark over phosphorus pentoxide. It is very soluble in water; 1 cc. of a water solution saturated at 0° contains 0.92 ± 0.02 g. The density (d_4^0) of such a solution is 1.209 ± 0.003. The solubility of benzoylformic acid in 10 cc. of carbon tetrachloride is 0.04 g. at 0°; 0.1 at 15°; 0.4 at 35°; 0.8 at 40°; 1.1 at 43°; 1.9 at 45°; **3.3** at 47.5° and 7.9 g. at 52". That the acid was pure was evidenced by sharp freezing point and correct titration values. The freezing point of the acid was found to be 64.85 * 0.05° (corr.).[1]

Careful work on benzoylformic acid must be done in diffused light since the acid is light, sensitive both in the solid state and in water solution.[2] A $N/10$ water solution, exposed to direct sunlight, acquired a strong benzaldehyde odor in about ten minutes and within twenty minutes the solution (at first clear) had become cloudy. After two hours, small drops of oil were seen floating on the surface and after several days of exposure to light large reddish-brown drops of oil had settled on the bottom of the flask. A $N/10$ solution of acid which was kept in the dark remained clear and developed no benzaldehyde odor in twenty-four hours. The fall in acidity, due to exposure to light, was followed by titration. In one case there was a 19.4% decrease in acidity in the first two hours and an additional 8% during the next two hours. There was no loss in acidity when a similar solution was kept in the dark. That benzaldehyde was present in the rayed sample was evident from the odor; also, benzaldehyde phenylhydrazone was isolated and its identity established by a mixed melting point comparison with an authentic sample.

An attempt was made to devise a gravimetric method of analysis for benzoylformic acid. Its phenylhydrazone was precipitated in various acidities by means of phenylhydrazinc hydrochloride and the yield determined. The best yield, 98.1 * 0.2%, was obtained in the presence of a small excess of hydrochloric acid. With increase in acidity the yield gradually fell; in 20% hydrochloric acid the yield was 84.7%. On the other hand, any decrease in hydrochloric acid below the one equivalent corresponding to the phenylhydrazine resulted in a sticky product which could not be filtered. Precipitation does not occur in alkaline solution, the phenylhydrazone of benzoylformic acid being soluble even in sodium carbonate.

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[1] Glücksmann, *Monatsh.*, 11, 249 (1890), reports the melting point as 65"; Claisen, *Ber.*, 10,431, 847 (1877), as 65-66°; Acree, ***Am. Chem. J.***, 50,391 (1913), as 63-64".

[2] Claisen ***[Ber.***, 10, 846 (1877); 12, 627 (1879)] observed that the solid acid (and also the ammonium salt) became yellow on exposure to light.

Four derivatives of benzoylformic acid—semicarbazone, thiosemicarbazone, *p*-nitrophenylhydrazone and 2,4-dinitrophenylhydrazone—were prepared in the hope of obtaining a derivative more suitable for gravimetric estimation than the phenylhydrazone but the last named seemed to be the best.

Experimental Part

Preparation and Purification.——Methyl (n^{24}_{D} 1.5208) and ethyl benzoylformate (n^{23}_{D}, 1.5102)[3] were the starting materials for the preparation of the acid. The ester was hydrolyzed at room temperature with aqueous sodium hydroxide. The resulting alkaline solution was strongly acidified with sulfuric acid, cooled and finally extracted with ether several times. The ether extract was dried with anhydrous sodium sulfate and filtered. The ether was evaporated and the residual oil warmed in a vacuum at ±60° for two hours. On standing overnight the oil solidified to a crystalline mass. The acid was crystallized seven times from carbon tetrachloride. The final product was freed from solvent by heating to incipient fusion in a current of dry air.

Carbon bisulfide was previously used[4] for crystallizing benzoylformic acid. Carbon tetrachloride, however, is more efficient in removing benzoic acid, which is the most probable impurity. This conclusion was reached after comparing the solubility curves of benzoylformicand benzoic acids in carbon bisulfide and carbon tetrachloride.

Benzoylformic acid has a slight odor. After handling this acid for several days one's fingers turn black and peel. The skin also turns black and peels when working with mandelic acid ($C_6H_5CHOHCOOH$), which is the starting material in the preparation of benzoylformic acid.

Solubility in Carbon Tetrachloride and in Water.—All solubilities in carbon tetrachloride except two were determined in a 20-cc. test-tube fitted with a cork which held a thermometer and which was nicked to allow a wire stirrer to be raised up and down. Ten cc. of solvent was placed in the tube and then weighed amounts of substance were added. Each addition was first brought into solution and then partially precipitated by cooling with rapid stirring. Finally, the tube was slowly warmed, with stirring, and the temperature noted at which the cloudiness (due to finely divided solid) disappeared. In the case of 0 and 52°, a 10-cc. portion of the saturated solution was evaporated and the solid weighed.

The solubility in water at 0° was determined by titrating a 1-cc. portion with *N*/10 sodium hydroxide. The density was measured according to Mulliken.[5] Scarcity of material prevented more accurate work. Concentrated solutions of benzoylformic acid in carbon tetrachloride and in water are yellow; dilute solutions are colorless.

Freezing Point.—The apparatus was essentially a small-scale Beckmann freezing point apparatus. It consisted of a 20-cc. test-tube equipped with a thermometer[6] and wire stirrer, the tube being jacketed with a slightly larger test-tube. Since benzoylformic acid is hygroscopic, entrance of moisture was prevented by blowing a gentle stream of dried air into the mouth of the inner test-tube. The cooling curve was plotted, temperature against time. After 0.5–1° supercooling, the temperature of the

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[3] Corson, Dodge, Harris and Hazen, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1928**, Vol. 8, p. 68.

[4] Acree, *Am. Chem.* J., 50, 391 (1913).

[5] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, **1914**, Vol. I, p. 229.

[6] This thermometer was compared with one which had been calibrated by the U. S. Bureau of Standards,

freezing acid quickly rose to 64.85 ± 0.05° and remained constant until practically all the sample had solidified. In a typical run the liquid supercooled to 63.5° and then the temperature rose to the plateau where it remained for three minutes at 64.87" and four minutes at 64.83". By this time the liquid was almost completely frozen and the temperature began to drop rapidly.

Titration.—The dissociation constant for benzoylformic acid at 25° as determined by Bader[7] by the conductivity method is 6 X 10^{-2}. According to Bjerrum's calculations of hydrolysis[8] a $N/10$ solution of the sodium salt of an acid of K_A, 6 X 10^{-2}, would have a PH of 7.5. We titrated the purified acid ($N/10$ solution) with $N/10$ sodium hydroxide to an end-point of PH 7.5 using phenol red as indicator and found the acid to be pure within 3 parts per 1000.

Anal. Calcd. for $C_8H_6O_3$: 0.2833 g. requires 15.31 cc. of 1.233 $N/10$ NaOH. Found: 15.35 cc.

Photochemical Decomposition.—We followed the decomposition of two samples of ± $N/10$ benzoylformic acid (tightly stoppered), one exposed to sunlight and the other kept in the dark. The procedure was to titrate 10-cc. samples with $N/10$ sodium hydroxide after various lengths of time.

SOLUTION EXPOSED TO LIGHT

Time	Hours	$N/10$ NaOH, cc.
11:35 A. M.	0	7.22
1:35 P. M.	2	5.82
2.35 P. M.	3	5 54
3:35 P. M.	4	5.24

SOLUTION KEPT IN THE DARK

Time	Hours	$N/10$ NaOH, cc.
11:35 A. M.	0	7.23
1:35 P. M.	2	7.23
5:35 P. M.	6	7.24
8:35 A. M.	21	7.25

The presence of benzaldehyde was proved by isolation of benzaldehyde phenylhydrazone. Since both benzaldehyde and benzoylformic acid precipitate phenylhydrazone when treated with phenylhydrazine reagent in the usual way, the normal procedure was modified so as to yield only benzaldehyde phenylhydrazone. This was easily accomplished by precipitating the hydrazone in the presence of a slight excess of sodium hydroxide. Under these conditions only the phenylhydrazone of benzaldehyde precipitated, the phenylhydrazone of benzoylformic acid remaining in solution as sodium salt.

In several cases another decomposition product was noticed, a very small quantity of a tan-colored, oily solid which floated on the top of the solution. The quantity was too small for identification. After drying on a clay plate and washing with petroleum ether, it melted from 90 to 110°. It bubbled a little when moistened with sodium carbonate solution but this acidity might have been due to adhering benzoylformic acid.

That benzoic acid was present was shown as follows. A rayed sample was extracted with ether and the ether, in turn, with sodium carbonate solution. The sodium carbonate was washed with ether and then acidified. The precipitated solid, after recrystallizing from water, was identified as benzoic acid. The amount was small and was very likely due to the air oxidation of the primary product, benzaldehyde. Presumably the decomposition brought about by light is $C_6H_5COCOOH \longrightarrow CO_2 + C_6H_5CHO$. Further work along this line is in progress in this Laboratory.

Gravimetric Estimation.—A method of analysis[9] for benzoylformic acid has been described in which the phenylhydrazone was precipitated with phenylhydrazine acetate

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[7] Bader, *Z. physik. Chem.*, 6, 289 (1890).

[8] Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1929, Vol. II, p. 828.

[9] Evans, *Am. Chem. J.*, 35, 123 (1906).

solution, After standing for twenty-four hours, the product was dissolved in sodium carbonate solution and reprecipitated with dilute sulfuric acid; the hydrazone was finally crystallized from hot benzene.

We were interested in developing a simpler procedure. Using phenylhydrazine hydrochloride as reagent the resulting phenylhydrazone was of such purity that recrystallization was unnecessary. A 98.1 ± 0.2% yield was consistently obtained according to the following directions. To a water solution of benzoylformic acid (25 cc. contains 0.25 g. of acid) was added 25 cc. of hydrazine reagent containing 0.48 g. (100% excess) of recrystallized phenylhydrazine hydrochloride and 0.5–5.5 cc. of *N*/5 hydrochloric acid. The mixture immediately became cloudy and within a few seconds was semi-solid with the lemon-yellow precipitate of benzoylformic acid phenylhydrazone. After standing for ten minutes, the mixture was filtered through a fretted glass Gooch crucible. The Gooch was dried in a vacuum desiccator containing both phosphorus pentoxide and stick sodium hydroxide (the latter to absorb hydrochloric acid). The hydrazone cannot be heated in an oven, even at 100° without some decomposition. Also, when concentrated sulfuric acid is used in the vacuum desiccator, the hydrazone changes from butter-yellow to dark brown and becomes sticky. Using the above procedure the yields are consistent and therefore benzoylformic acid can be determined gravimetrically provided the factor 100/98.1 is employed.

Derivatives.—The method of preparation was the same in all cases. To a water solution of the acid was added a water solution (usually hot) of the hydrochloride of the reagent in question. The solid product quickly appeared. These products are soluble in the usual organic solvents and they are also moderately soluble in water. They decompose at the melting point and the melting point depends somewhat on the speed of heating. Of the four derivatives prepared only two—thiosemicarbazone and 2,4-dinitrophenylhydrazone— are new.

Benzoylformic Acid **Thiosemicarbazone.**—This substance crystallizes from acetic acid or water as a pale yellow solid. It melts at 188–189° (corr.) with decomposition.

Anal. Calcd. for $C_9H_9O_2N_3S$: C, 48.4; H, 4.0; S, 14.4. Found: C, 47.8; H. 4.2; S, 14.0.

Benzoylformic Acid **2,4-Dinitrophenylhydrazone.**—The yellow product was crystallized from acetic acid. It melts at 196–197" (corr.) with decomposition.

Anal. Calcd. for $C_{14}H_{10}O_6N_4$: C, 50.9; H, 3.0. Found: C, 50.8, 51.0; H, 2.9, 2.8.

Summary

The solubility of benzoylformic acid in carbon tetrachloride at several temperatures and in water at 0° has been determined—also the density of the latter solution. The pure acid freezes at 64.85 ± 0.05°. A *N*/10 water solution of the acid decomposes slowly when exposed to sunlight. Benzoylformic acid phenylhydrazone may be used under certain conditions in the gravimetric estimation of the acid. Two new derivatives are described.

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[CONTRIBUTION FROM THE DIVISION OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

THE STRUCTURE OF METHYLATED SUGARS. II[1]

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On looking over the literature on the methylation of simple sugars, it is seen that the so-called gamma or active or unstable derivatives have been obtained from solutions at comparatively low temperature and low concentration of acid. Except in the first paper of this series,[3] the active monomethyl derivative has never been made by the methyl sulfate method. It * has had to be isolated from other preparations before further methylation.

Since low temperatures and nearly neutral solutions appear to be the least drastic and most normal conditions under which methylation can take place, it seemed desirable to determine whether the product obtained by methylating simple sugars under these conditions is a stable or unstable form.

Mannose was selected for the present investigation because previous work by one of us[4] indicated that under conditions similar to those here considered, mannose formed a product which could not be completely methylated by the methyl sulfate method.

One of the most characteristic properties of the methyl derivatives of unstable sugars is the speed of reaction with potassium permanganate. There is considerable confusion in the use of this test because some writers specify alkaline permanganate solution, while others specify neutral permanganate and still others do not specify whether the solution is alkaline, neutral or acid. The test is not generally used in a way that is even semi-quantitative.

A method has been developed[5] for determining the rate of oxidation of various sugars and hexosides by means of potassium permanganate in an acid buffered solution. This method seems not to have been applied previously to alkyl derivatives of either stable or unstable sugars and it seemed desirable to apply it to these derivatives.

Apparatus

The two pieces of apparatus deserving particular description are the methylator and the vacuum distilling apparatus.

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[1] This paper is taken from a thesis submitted by John E. Milbery in partial fulfilment of the requirements for the degree of Master of Science in the Department of Chemistry in the Graduate College of the State University of Iowa.

[2] Kansas State Agricultural College, Manhattan, Kansas.

[3] Whitnah, THIS JOURNAL, 51, 3490 (1929).

[4] C. H. Whitnah, "Studies in the Structure of the Lactones of Sugar Acids," University of Nebraska Thesis, 1925, p. 9.

[5] Kuhn and Wagner-Jauregg, Ber., 58, 1441 (1925).

The reaction flask of the methylator was an ordinary 2-liter pyrex balloon flask **(A).** This was fitted with a rubber stopper through which extended one end of a condenser (L), electrodes of antimony and platinum (Sb, Pt) and the two buret tips (M,N). There was also a small hole in the stopper used in removing the samples used for indicator tests.

This flask was immersed to about half its depth in a simple constant temperature bath made from an ordinary pneumatic trough. The bath was heated by an electric lamp which was controlled by a mercury thermoregulator and relay. The bath was agitated by jets of air from a glass tube in which several small openings had been drawn out. The temperature variation was too small to be detected by an ordinary thermometer graduated in single degrees.

The methylator was originally constructed for handling larger quantities of sugar at higher temperatures where the reaction was rapid. For this reason the burets (B,C) were large and were so arranged that a comparatively constant head of liquid might be maintained even though the volume of liquid was decreasing. These burets were filled by placing the tubes (R) and (T), respectively, in a flask of the reagent and applying suction at (H) or (K). Before the end of the work here reported, the sodium hydroxide buret was replaced by an ordinary 50-cc. buret which was sealed to the bent tube at the point (X).

The stirrer (S) was passed through the condenser to a motor mounted above.

The electrode (Sb) was made by pouring molten antimony into a sealed glass tube and then dipping a copper wire into it. When the antimony had become solid, the glass was broken from the end of it, leaving a rod of antimony sealed into the glass tubing. The electrode (Pt) consisted of a platinum wire welded to a copper wire and sealed through a glass tube.

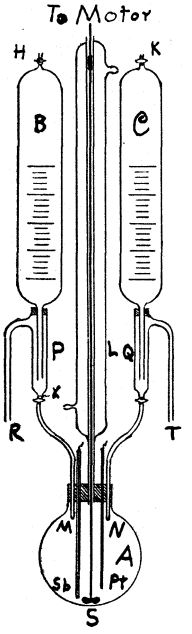


Fig. 1.—Methylator.

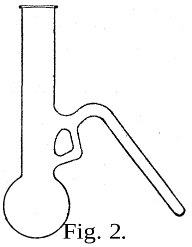


Fig. 2.

The arrangement of methylator and wiring for thermostat and potentiometer is indicated by Fig. 1.

The vacuum distillation apparatus consisted of an oil-sealed pump, a mercury manometer of the U type, a two-pronged adapter, which made it possible to collect two fractions without disturbing the vacuum, a short water-cooled condenser and a special 25-cc. distilling flask (Fig. 2) which prevented the liquid from bumping over into the condenser.

Experimental Part

The mannose used in this work was prepared from ivory nut shavings by a slight modification of Harding's method,[6] the shavings being supplied by the Rochester Button Co. The crystalline product used for methylation melted at 125–126° uncorrected and gave a specific rotation of 16.6° five minutes after solution. The product was found to be free from both barium and sulfate. The crystals were white and dissolved in water to form a transparent colorless solution.

[6] Harding, Sugar, 25, 583 (1923).

Methylation of Mannose. All methylations were carried out in the general manner now to be described. The particulars of each significant run are shown in Table I.

The bath was adjusted to the desired temperature and the burets were filled. Then the sugar was dissolved and poured into the flask through the hole from which samples for titration were withdrawn. A little dimethyl sulfate was then added and the solution adjusted to the desired alkalinity by the addition of 30% sodium hydroxide. The alkalinity was tested by adding a drop of solution to a drop of indicator on a spot plate and then adding drops of solution and dilute acid as necessary. Since relatively large quantities of indicator had to be used, enough sodium hydroxide was added to the phenolphthalein solution to give it the faint pink color of the end-point. Each drop of brom thymol blue, which is insoluble in neutral solution, was neutralized on the spot plate.

When the alkalinity had been adjusted, it was kept near this point by adding a drop of alkali from time to time as required. The alkalinity was also checked with some success by means of the electrode–potentiometer arrangement. The potentiometer was so set that there was no deflection of the galvanometer when the mixture was at the desired alkalinity. Alkali was added as soon as the needle swung to the acid side. If the electrical control worked at all, it was much more sensitive and convenient than the indicator method. Occasional checking by the indicator method was always necessary, however, and at times the electrical control was very erratic.

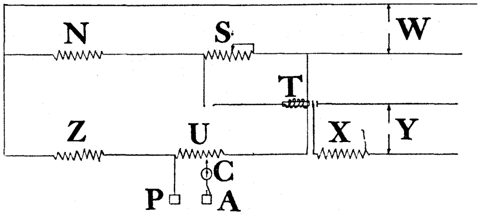


Fig. 3.—Wiring diagram. N, 30 c.p. 110 v. lamp; S, 30 ohms; W, 110 v. d.c.; T, thermostat relay; Z, 20 c.p. 220 v. lamp; U, 6 ohms; X, heating lamp; Y, 110 v. a.c.; C, galvanometer key; P, platinum; A, antimony.

The reaction was considered to be practically complete when a marked decrease occurred in the rate at which sodium hydroxide was required. The last traces of methyl sulfate were then removed either by heating or by long continued action of alkali at the temperature of methylation.

When constant alkalinity showed the destruction of methyl sulfate to be complete, the solution was cooled if necessary and extracted twice with 75-cc. portions of chloroform. The aqueous residue was then made faintly acid with dilute sulfuric acid and extracted twice more.

The combined chloroform extracts were dried by shaking with lumps of calcium chloride, decanted from the drying agent and the chloroform was distilled off on a water-bath. The sirup which remained was transferred to the special distilling flask with the aid of a little chloroform.

The last traces of chloroform were then removed by heating to about 100° in an oil-bath and applying suction from a water pump. The suction was then changed with the aid of a three-way cock to an oil-sealed mechanical pump. After the pressure became suitably reduced, the temperature of the oil-bath was gradually raised until the product distilled at the temperature and pressure shown in Table I.

In Table I the following abbreviations are used: Pot. = readings on arbitrary scale of potentiometer; PP = reaction toward phenolphthalein; BTB = reaction toward brom thymol blue; NaOH = number of cc. of 30% sodium hydroxide added; Me_2SO_4 = number of cc. of dimethyl sulfate added; under the columns headed PP and BTB, N = neutral, N--A =

TABLE I

METHYLATION OF MANNOSE

Run no.	2	5	8	9	10
Reagents	**50** cc. H_2O; **20** g. sirup	**50** cc. H_2O; **20** g. crystals	**30** cc. H_2O; **10** g. crystals	**50** cc. H_2O; **20** g. crystals	**50** cc. H_2O **20** g. crystals
Temp. **1** (during reaction)	50° for **2** hrs.	30° for **14** hrs.	**30"** for **17** hrs. before reagents **added;** 30–40° in 1 hr.; 40° 6.5 hrs.	30° for **18** hrs.	35° for **11** hrs.
2 (final)	100° 0.5 hr.	30° until titer constant	40° until titer const.	30° until titer const.	35° until titer const.
Yield °C./mm.	**10.4** g., **49.3%** CH_3O 116–128/2	**3.5** g., **52.7%** CH_3O 122–124/1	Fr. I, **2.8** g., **52.5%** CH_3O 95–105/0.5 **Fr. II, 1.3** g., **50.0%** CH_3O 105–115/0.5	Fr. I, **1.9** g., **52.7%** CH_3O 115/1–7 Fr. II, **5.7** g., **52.5%** CH_3O 99–100/1	**Pr. I, 3.9** g., **54.2%** CH_3O 95–101/0.5 Fr. II, **7.7** g., **52.5%** CH_3O 101–115/0.5
Form	Stable	Unstable	Stable	Unstable	Stable

Time	P. P.	NaOH	Me_2SO_4	Pot.	P. P.	BTB	NaOH	Me_2SO_4	Pot.	P. P.	BTB	NaOH	Me_2SO_4	P. P.	BTB	NaOH	Me_2SO_4	P. P.	BTB	NaOH	Me_2SO_4
0:00	1/2	0	0		**A**	**B**	0	0		**N**	**B**	0.0	0	B	B	0.0	0	A	A	0.0	0
0:14	1/1	7	5		**A**	**N-B**	6	45		**N-A**	**B**	0.4	6	B	B	3.7	53	A	B	5.1	58
0:22	1/1	19	15							**A**	**N**	0.6		A	B	3.7		A	B	5.3	
0:30	1/2	26	24	120	**A**	**B**	7			**A**	**B**	0.8		A	B	4.0		A	B	6.2	
1:00	2/1	54	47							N	B	1.5		A	B	5.1		**A**	**B**	7.9	
1:30	N	86	82	107	**A**	B	10	49	110	N	**B**	4.8	17	A	B	5.8		**A**	**B**	10.0	
2:00	2/1	114 end	100	105	**A**	**B**	11		91	**N-A**	**B**	9.0		A	B	6.6		**N-A**	**B**	11.9	
2:30				99	**A**	N-B			91	A	B	11.0		A	N	7.3		**A**	B	14.8	74
3:00				103	**A**	**B**	11.5		91	A	B	17	31	A	B	8.5		A	B	17.9	
3:30				103	**A**	**B**	14		88	A	N	20	32	A	B	9.3		A	N	21.1	
4:00				97	**A**	**B**	16		88	A	B	25	34	A	B	10.0	93	N	B	24.8	
5:00				97	**A**	**B**	17		85	N		40	46	A	B	14.0		N-A		32.8	
6:00				97	**A**	**B**	20		94	1/3		56	52	A	N	16.0		N		39.7	
7:00									112	N		83	76	A	B	18.0		1/3		48.6	94
7:45				97	**A**	N	24		112	1/3		95		A	B	19.5		N		67.6	114
8:35				107	**A**	N	29							**A**	**B**	21.5		1/4		89.7	
9:00				103		**N-B**	30			1/2		96 end		**A**	**B**	22.6		N		101.0	140
10:00				97		**N-B**	34							**N-A**		26.6		N		138.0	
10:45				93	**N-B**		36							**N**		30.6					
11:30				87	1/1		45							1/2		37.2		1/1		178.0end	
13:05				95	1/1		98	89						N-B		55.5					
13:35				95	1/1		127	131						1/2		66.6					
13:55					1/1		144 end							N-B		72.9	114				
16:11														1/4		134.0	139				
17:53														1/2		166 end					

neutral to acidic, A = acidic, N-B = neutral to basic and B = basic. The denominators of the fractions in these columns indicate the number of drops of solution required to neutralize the number of drops of 0.025 N hydrochloric acid indicated by the numerators. Hence the larger the value of the fraction, the more alkaline the solution.

Runs 6 and 7, which are mentioned in the report of oxidations (Table II) but are not included in Table I, were on crystalline mannose at 50 and 40°, respectively. Run 10 shows that they were not significant to the present problem.

It must be understood that the alkalinity required testing very frequently and that the observations recorded are typical instances.

The unstable products are distinguished from the stable by speed of reaction with neutral permanganate, speed of reaction with buffered acid permanganate, greater mobility when fresh, greater discoloration and much greater viscosity after standing for a few weeks.

Oxidation Experiments.—The modifications in the method of Kuhn and Jauregg were mainly for the purpose of adapting the method to smaller quantities of material.

The calibration of volumetric apparatus did not seem justified in the present work. The same instruments, however, were used in all runs and the buret used in thiosulfate titrations was filled to the zero mark each time.

An approximately 0.1 N solution of potassium permanganate was allowed to stand until its concentration became sensibly constant and then standardized against sodium oxalate as 0.1026 N. This solution was used in all runs.

Approximately 0.02 *N* solutions of sodium thiosulfate were made and titrated against the permanganate solution in buffered potassium iodide, the exact procedure being followed that was used in oxidation experiments.

The phosphate buffer was made up so as to be approximately *M*/15 with respect to both phosphoric acid and primary potassium phosphate. The actual quantities were 5.0 cc. of H_3PO_4 (85%) and 9 *g.* of KH_2PO_4 per liter of solution. The P_H of this solution after being diluted five times, as was the case in the oxidations, was determined colorimetrically to be **2.3.** No difference could be observed in the P_H of a solution in which oxidation had been allowed to continue until the permanganate had been destroyed.

A 10% solution of potassium iodide was made up by weight and replaced whenever it became slightly yellow.

The experimental procedure was as follows: 20 cc. of the buffer solution was run from a buret into a 100-cc. volumetric flask and placed in a thermostat at 30°. The permanganate was then added from a pipet. When this mixture had come to temperature, the substance to be tested was added and the solution quickly made up to volume with water at 30°. When studying the effect of time in solution on rate of oxidation, 5 g. of substance was weighed out and made up to 250 cc. of solution. This solution was kept in the bath at **30°** and 50 cc. used for each oxidation. When the initial rate only was desired, exactly 1 g. of substance was dissolved and then added to the oxidizing solution.

At definite time intervals after starting the oxidation 10-cc. samples were removed with a pipet and run into flasks containing 15 cc. of buffer solution and 1 cc. of potassium iodide solution. The liberated iodine was immediately titrated with thiosulfate, starch indicator being used near the end-point.

TABLE II

OXIDATION OF SUGARS IN BUFFERED POTASSIUM PERMANGANATE

	Minutes of oxidation	1	2	3	6	7	10	12	20	30	40	50	60	70
Substances oxidized	$KMnO_4$ added, cc.	Volume in cc. of 0.1026 *N* $KMnO_4$ decomposed in minutes shown above												
1.1027 g. glucose	10						0.66		3.14	6.48	6.64	6.82	6.86	
1.0209 g. glucose	10						.32		1.60	4.10	6.60	6.71	6.82	
Glucose; 2:55 hr.	10						.44		0.78	1.06	1.36	1.76	2.12	2.40
Glucose; 23:05 hr.	10						.30		.46	0.68	0.86	1.14	1.44	1.72
Glucose; 40:05 hr.	10						.38		.56	0.70	0.86	1.10	1.42	1.72
Mannose; 0:15 hr.	10						.48		.84	1.42	1.80	2.40	3.04	3.66
Mannose; 42:05 hr.	10						.42		.64	1.00	1.42	1.80	2.36	2.80
Product of Run 2	10						.84		1.22	1.48	1.74	1.94	2.20	2.36
Same; 30:10 hr.	10						.84		1.24	1.54	1.80	2.04	2.28	2.50
Same; 47:40 hr.	10						.80		1.22	1.54	1.80	2.00	2.26	2.52
Fraction I, Run 6	10						.40		0.50	0.62	0.78	0.88	1.04	1.12
Fraction I, Run 7	10						.36		.46	.58	.76	.88	1.02	1.14
Fraction I, Run 8	10						.42		.54	.64	.76		1.04	
Fraction I, Run 10	10						.44		.58	.68	.76	.90	1.06	
Fraction II, Run 6	10						.26		.46	.54	.76	.84	0.94	1.14
Fraction II, Run 7	10						.26		.44	.56	.70	.80	.94	
Fraction II, Run 10	10						.20		.40	.54	.72	.82	.92	
Product of Run 5	10			9.46		9.72	..	9.92						
Same; 0.1044 g.	10				2.86	2.91	3.02	3.10	3.34	3.55	3.65	3.74	3.86	3.95
Fraction II, Run 9	20	17.30			18.26		..	18.64						
Same (2d distillation)	20		14.24			15.44	..	15.76	16.08					

The volume of permanganate reduced by the substance was then calculated and is shown in Table II.

The first two determinations on glucose were made without the buffer and clearly show the variable results obtained without buffer.

Summary and Conclusions

The character of the products obtained by methylating mannose with dimethyl sulfate and sodium hydroxide at temperatures between 30 and 50" has been studied.

A sirup having the analysis and properties of trimethyl-γ-methylmannoside was formed in a solution between P_H 7.0 and 8.5 at a temperature of 30°. The product formed on similar treatment at 35° had no gamma properties and was a mixture of sugar methylated to varying degrees.

The method of Kuhn and Jauregg for studying the rate of oxidation of sugars by permanganate was applied to the oxidation of polymethyl methyl mannosides. The results showed clearly the very great difference in the behavior of stable and unstable forms toward potassium permanganate.

MANHATTAN, KANSAS

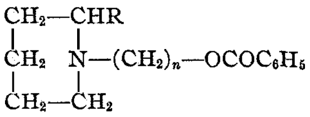
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

PIPERIDINE DERIVATIVES. VIII. SUBSTITUTED PIPERIDINO-ALKYL BENZOATES

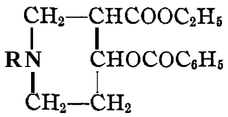
BY C. F. BAILEY AND S. M. MCELVAIN

RECEIVED DECEMBER 20, 1929 PUBLISHED APRIL 7, 1930

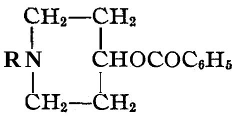
In a previous communication[1] from this Laboratory a number of substituted piperidino-alkyl benzoates (Type I) were reported. It was found that when a methyl group substituted the 2- or 3-position of the piperidine nucleus, a much more effective local anesthetic was produced than when the piperidine nucleus remained unsubstituted or was substituted by a *n*-propyl group or a carbethoxy group. Other types of structure which have been found to produce quite pronounced local anesthetic effect are the 1-alkyl-3-carbethoxy-4-piperidyl benzoates (Type II)[2] and the 1-alkyl-4-piperidyl benzoates (Type III).[3] In those cases in which the R of Types II and III is a phenylethyl group extraordinary local anesthetic action is shown.



I



II



III

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[1] McElvain, THIS JOURNAL, 49, 2835 (1927).

[2] McElvain, *ibid.*, 48, 2179 (1926); Thayer and McElvain, *ibid.*, 49, 2862 (1927).

[3] Bolyard and McElvain, *ibid.*, 51, 922 (1929).

On account of the efficiency of the methyl group as a substituent in compounds of Type I, it seemed desirable to prepare the 4-methyl isomers of the 2- and 3-methylpiperidino-alkyl benzoates. Also it was reasonable to expect that certain phenyl-alkyl groups, such as had proved valuable in compounds of Types II and III, would enhance the pharmacological properties of Type I when they were substituted in the piperidine nucleus.

Accordingly the following substances have been prepared and submitted for pharmacological study: (1) 4-methylpiperidino-ethyl benzoate, (2) 4-methylpiperidino-propyl benzoate, (3) 2-benzylpiperidino-propyl benzoate, (4) 2-phenylethylpiperidino-ethyl benzoate, (5) 2-phenylethylpiperidino-propyl benzoate, (6) 4-phenylethylpiperidino-ethyl benzoate.

These esters were prepared by the condensation of the correspondingly substituted piperidine with β-chloro-ethyl benzoate and y-chloropropyl benzoate. It should be pointed out that the 2-phenylethyl- and 2-benzyl-substituted piperidines condense with the chloro esters with much more difficulty than the 4-phenylethylpiperidine. A similar difference in reactivity was noted[1] in the case of 2-methyl- and 3-methylpiperidine. All of the piperidino-alkyl benzoates were isolated and purified as the hydrochlorides with the exception of the 2-phenylethylpiperidino-ethyl benzoate (4). No salt of this amino ester could be induced to crystallize. The free base was finally purified by distillation under diminished pressure.

In the preparation and crystallization of 2-phenylethylpiperidino-propyl benzoate hydrochloride, two distinctly different compounds were obtained. They are probably geometric isomers.[4] One of these compounds melts at 123–125° and the other at 149–151°. The ratio in which they are formed seems to be dependent upon the temperature at which the tertiary amino ester is formed. At lower reaction temperatures both isomers appeared, but at higher reaction temperatures only the higher-melting isomer was isolated. It will be seen from the pharmacological data that these two compounds show a distinctly different physiological activity.

The 4-methylpiperidine that was used was obtained by the reduction of γ-picoline. This latter compound was obtained rather unexpectedly in an attempt to isolate β-picoline from coal tar bases. It was thought that the fraction boiling at 142–146° obtained by the fractionation of the "Denaturing Pyridine" of Barrett and Company would contain a mixture of β- and y-picoline along with some 2,6-dimethylpyridine and possibly other higher-boiling dimethylpyridines. A statement by Meyer and Jacobson[5] that β-picoline could be separated from the a- and y-isomers by treatment of the mixture with benzaldehyde and zinc chloride followed by the removal of the unchanged β-picoline from the condensation products of the a- and γ-isomers (a- and γ-stilbazole) suggested the possibility of the fraction of the

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[4] Cf., Mills, Parkin and Ward, J. Chem. *Soc.,* 2613 (1927).

[5] Meyer and Jacobson, "Lehrbuch der Organischen Chemie," 1920, Vol. *2* [3], 807.

coal tar bases boiling at 142–14G° being a source of β-picoline. After treatment of this fraction with benzaldehyde in the presence of zinc chloride, a base boiling at 140–145° and thought to be β-picoline was recovered from the reaction mixture. The recovered product amounted in weight to about 35% of the crude basic fraction that was taken. This recovered base, however, was shown to be fairly pure y-picoline rather than β-picoline by the fact that on oxidation it yielded isonicotinic acid, m. p. 304–306° (nicotinic acid melts at 228–229°), and also formed a picrate which melted at 158–161°.[6] The picrate of synthetic β-picoline melted at 144–147° and a mixed melting point of the two picrates was 127–135°.

It appears from these results that the 142–146° fraction from this particular mixture of coal tar bases contains very little β-picoline, and that under the conditions used the y-picoline which is present does not condense to any great extent with benzaldehyde. Because of these facts this particular mixture of coal tar bases can be recommended as a very satisfactory source of y-picoline. In this connection it is interesting to note that Freudenberg[7] has pointed out that the nicotinic acid prepared by Hess and Leibbrandt[8] by the oxidation of supposed β-picoline from coal tar bases was mainly isonicotinic acid resulting from the oxidation of γ-picoline.

2-Benzylpiperidine was obtained by the catalytic reduction of α-benzylpyridine. The 2- and 4-phenylethylpiperidines were prepared by the catalytic reduction of a- and y-stilbazoles.

Experimental

γ-Picoline from Coal Tar Bases.—The "Denaturing Pyridine" of Barrett and Company was fractionated twice through a 45-cm. column packed with glass rings. The following fractions were taken: up to 120°, 120–126°, 126–130°, 130–135°, 135–142°, 142–146°, above 146". A mixture of 186 g. of the 142–146° fraction, 212 g. of benzaldehyde and 272 g. of pulverized, freshly fused zinc chloride was heated under a reflux condenser in an oil-bath at 200–210° for twenty to twenty-four hours. Sufficient concentrated solution of sodium hydroxide was then added to insure complete decomposition of the zinc chloride and the mixture steam distilled until the distillate failed to show a basic reaction to litmus paper. By this time the distillate amounted to 4-6 liters. Hydrochloric acid was added to the distillate until it showed an acid reaction to congo red paper. The acid solution was then evaporated to dryness on a steam-bath. The free base was liberated from its salt with concentrated sodium hydroxide. It separated as an oil which, after drying over solid potassium hydroxide, boiled at 140–145'. The yield was 55–65 g. (30–35% of the original amount of mixed bases).

The picrate of this material was prepared by adding 0.5 cc. of the base to a solution of 0.5 g. of picric acid in 15 cc. of alcohol. After two recrystallizations from alcohol the picrate melted at 158–161°. The picrate made from a sample of synthetic β-picoline,

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[6] Mulliken, "Identification of Pure Organic Compounds," 1916, Vol. II, p. 139, gives 167° as the melting point of the picrate of y-picoline.

[7] Freudenberg, Ber., 51, 1668 (1918).

[8] Hess and Leibbrandt, *ibid.*, 50, 385 (1917).

prepared by the method of Schwarz,[9] melted at 144–147°. The melting point of a mixture of these two picrates was 127–135°.

A 15-g. sample of the y-picoline was oxidized at 70° with 51 g. of potassium permanganate in about 500 cc. of water. After the reaction was complete, the precipitated manganese dioxide was filtered off and the clear filtrate evaporated to about one-half its volume and then made just neutral with sulfuric acid. The correct amount of a copper sulfate solution was then added to precipitate the copper salt of the acid. Seven g. of this salt was obtained. The copper salt was suspended in 200 cc. of hot water and the copper removed by precipitation with hydrogen sulfide. After filtering off the copper sulfide the filtrate was concentrated and the isonicotinic acid allowed to crystallize. After recrystallization 2.9 g. of the acid that melted at 304–306° was obtained.[10]

No attempt was made to isolate any of the benzaldehyde condensation products from the reaction mixture after the removal of the unchanged base.

α-Benzylpyridine.—This compound was prepared by the method of LaForge.[11] The product that was used boiled at 277.8–280°.

a-Stilbazole (Symmetrical **α-Pyridylphenylethylene**).—A mixture of 186 g. of the picoline fraction that boiled at 126–130°, 212 g. of benzaldehyde and 272 g. of pulverized freshly fused zinc chloride was heated for twelve to fourteen hours at 200–210° under a reflux condenser. Sufficient concentrated sodium hydroxide solution was then added to react with the zinc chloride and the mixture steam distilled to remove any unchanged picoline and benzaldehyde. The brown, tarry a-stilbazole was then extracted from the reaction mixture with benzene. After removal of the solvent by distillation, the α-stilbazole was distilled under diminished pressure. It boiled at 175–177° (3 mm.) and solidified in the receiver. After two recrystallizations from 70% alcohol it melted at 87–88.5°. The yield was 27–33 g.

The hydrochloride of this a-stilbazole melted at 176–177°.[12]

γ-Stilbazole (Symmetrical **γ-Pyridylphenylethylene**).—This compound has been prepared by Friedländer,[13] by heating γ-picoline, benzaldehyde and zinc chloride in sealed tubes at 220–230° for eight hours. When these conditions were tried an excessive amount of tar was formed from which it was practically impossible to isolate any of the desired y-stilbazole. It was found that heating for a shorter period of time at a somewhat lower temperature appreciably reduced this tar formation and increased the yield of the stilbazole. Accordingly the following procedure was used: six sealed bomb tubes, each containing 35 g. of y-picoline, 40 g. of benzaldehyde and 51 g. of zinc chloride were heated for three hours at 200°. The tubes were then opened, their contents combined and the γ-stilbazole isolated in the manner described above for a-stilbazole. The material boiling at 180–200° (3 mm.) was collected and recrystallized several times from 95% alcohol. A yield of 19.4 g. of product melting at 125–127° was obtained.

4-Methylpiperidine.—To a solution of 76 g. of γ-picoline in 1.5 liters of absolute alcohol contained in a 3-liter flask fitted with an efficient reflux condenser was added 227 g. of sodium over a period of one hour. After the addition of all of the sodium, a further 750 cc. of absolute alcohol was added and the mixture heated until all of the sodium had disappeared. The condenser was then set for downward distillation and the alcohol and base were distilled off. During this process 900 cc. of water was slowly

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[9] Schwarz, *Ber.*, **24**, 1676 (1891).

[10] The above oxidation of y-picoline was carried out by Mr. Mortimer C. Denison in the course of a study of the preparation of pyridine carboxylic acids by the oxidation of picolines. The details of this work will be the subject of a future communication.

[11] LaForge, THIS JOURNAL, 50, 2484 (1928).

[12] Cf. Baurath *Ber.*, **21**, 818 (1888).

[13] Friedlander, *ibid.*, **38**, 159 (1905).

added to the reaction mixture through a separatory funnel. The distillation was continued as long as the distillate showed a basic reaction. One hundred cc. of concentrated hydrochloric acid was then added to the distillate and the alcohol distilled off from a steam-bath. The hydrochloride of 4-methylpiperidine was obtained by evaporating the remainder of the solution to dryness. The free base was liberated with saturated sodium hydroxide solution, separated and dried over solid potassium hydroxide. Distillation of this material gave 56 g. (68%) of 4-methylpiperidine which boiled at 122–129°.

Several attempts were made to reduce the γ-picoline with Adams' platinum-oxide platinum black catalyst according to the procedure used' for the reduction of α- and β-picolines. There was some absorption of hydrogen but it soon stopped and could not be caused to continue either by activation of the catalyst or the addition of fresh catalyst.

2-Benzylpiperidine, **2-Phenylethylpiperidine** and **4-Phenylethylpiperidine.**—These compounds were obtained by the catalytic reduction of α-benzylpyridine, α-stilbazole and γ-stilbazole in alcoholic solution using a nickel catalyst at temperatures of 150–165° and at pressures of 150–200 atmospheres of hydrogen.[14] The physical properties of these substituted piperidines are given in Table I.

Table I

Physical Properties of Substituted Piperidines

Piperidine substituent	B. p., °C.	d_{20}^{20}	n_D^{25}	Hydrochloride m. p., °C.	Hydrochloride Analyses, % Cl Calcd.	Hydrochloride Analyses, % Cl Found
2-Benzyl	266.6–269	0.9749	1.5237	.....[a]	...	...
2-Phenylethyl	137.5–138.5 (3 mm.)	.9483	1.5207	156–158[b]	15.74	15.64
4-Phenylethyl	126–130 (3 mm.)	.9713	1.5293	171–173[c]	15.74	15.50

[a] The picrate was prepared. It melted at 154–156°. Tschitschibabin reported [Tschitschibabin, Chem. *Centr.*, II, 597 (1902)] 156–157° as the melting point of this picrate. [b] Baurath (Ref. 12) reported 155°. [c] Friedlander [Friedländer, *Ber.*, 38, 2837 (1905)] stated that this hydrochloride was an oil.

The phenylsulfonamides of 2-phenylethyl- and 4-phenylethylpiperidine were prepared. They melted at 129–130° and 130–131°, respectively (mixed m. p. 110–114°).

Anal. Calcd. for $C_{19}H_{23}O_2NS$: N, 4.26. Found: N, 4.26 and 4.04, respectively.

Substituted Piperidino-alkyl **Benzoates.**—These compounds were prepared by the general procedure of heating 2 moles of the substituted piperidine with 1 mole of β-chloro-ethyl benzoate or γ-chloropropyl benzoate. The 4-substituted piperidines could be caused to react by heating for one to three hours at 100–120°. These conditions, however, caused very little if any reaction in the case of the 2-substituted piperidines. It was necessary to use temperatures of 130–150° for at least six hours to cause them to condense. The tertiary amino esters with the exception of β-2-phenylethylpiperidino-ethyl benzoate, were isolated as the hydrochlorides, by the procedure previously employed' for compounds of this type. These hydrochlorides are summarized in Table II.

Numerous efforts were made to obtain a crystalline hydrochloride, hydrobromide and sulfate of the β-2-phenylethylpiperidino-ethyl benzoate. In all cases, however, these salts were obtained as thick oils which could not be induced to crystallize. Since this anesthetic was particularly desired for pharmacological comparison, it was purified as the free base by distillation under diminished pressure. It boiled at 202–207° (1 mm.).

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[14] This work was done by Mr. Howard Cramer under the direction of Professor Homer Adkins and will be described in detail by them in a forthcoming paper.

TABLE XI

SUBSTITUTED PIPERIDINO-ALKYL BENZOATE HYDROCHLORIDES

	Piperidino-alkyl group	M. p., °C.	Analyses, Cl % Calcd.	Found
1	β-4-Methylpiperidino-ethyl	181–184	12.52	12.43
2	y-4-Methylpiperidinopropyl	165–168	11.93	11.91
3	y-2-Benzylpiperidinopropyl	169–171	9.50	9.55
4	β-2-Phenylethylpiperidino-ethyl	Oil	...	...
5	y-2-Phenylethylpiperidinopropyl	123–125	9.16	9.11
6	γ-2-Phenylethylpiperidinopropyl	149–151	9 16	9.10
7	β-4-Phenylethylpiperidino-ethyl	163–165	9.50	9 32

Anal. Calcd. for $C_{22}H_{27}O_2N$: C, 78.29; If, 8.07. Found: C, 78.58, 78.21; H, 8.69, 8.58.

When **y-2-phenylethylpiperiditiopropyl** benzoate was prepared by heating together the secondary amine and the chloro ester at 140–150° for six hours, two different hydrochlorides were isolated. As the hydrochlorides were recrystallized from an alcohol–ether mixture it was noticed that one type of crystals formed as a somewhat discolored cake on the bottom of the flask, while in the supernatant liquid a flocculent precipitate of pure white, needle-like crystals appeared. These were separated by decanting the supernatant liquid which carried along the white crystals. These apparently different substances were recrystallized separately several times. The one which had appeared as a white flocculent precipitate was found to melt finally at 123–125° and the other at 149–151°. The melting point of a mixture of the two was indefinite, over a considerable range, but between the melting points of the individual compounds. From 12 g. of 2-phenylethyl-piperidine (2 mol.) and 6.3 g. of y-chloropropyl benzoate (1 mol.) were obtained in purified form 1.6 g. of the lower-melting compound and 2.1 g. of the higher-melting compound. If the reaction in which the tertiary amine was prepared were carried on for one hour at 200–210° the only product obtained was the higher-melting compound.

These two compounds are probably geometric iosmers but the evidence at hand does not warrant a definite conclusion on this point. Further work is contemplated in this direction.

Pharmacological Report

These benzoates are being studied pharmacologically by Mr. Charles L. Rose of The Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana. A brief report of this work is summarized in Table III. Each of the compounds is designated in this table by the number which is associated with it in Table II. In the case of No. 4 which was obtained as the free base a solution of the hydrochloride was prepared by titration of the base with standard acid. Anesthetic efficiencies were determined by application of a 2% solution of the hydrochloride to the rabbit's cornea and noting the duration of anesthesia. In some cases the infiltration anesthesia values as determined from intracutaneous injection into the guinea pig are reported. Subcutaneous toxicity to white mice and intravenous toxicity to white rats were determined. The corresponding values for cocaine (8) and procaine (9) are included in Table III for comparison.

Discussion of the Pharmacological Data.—A comparison of the

TABLE III

PHARMACOLOGICAL DATA

	Av. duration of anesthesia		Subcutaneous toxicity to white mice (mg./kg.)			Intravenous toxicity to white rats (mg./kg.)		
Compound	Rabbits cornea, minutes	Infiltration, minutes	M.T.D.	M.L.D.	No. of mice used	M.T.D.	M.L.D.	No. of rats used
1	11 (2% sol.)	..	1300	1400	..	40	42.5	12
2	14 (2% sol.)	..	..	..[a]	..	20	22.5	17
3	5-6 days (2% sol.) 13 min. (0.1% sol.)	71[b]	450	500	21	12.5	15	18
4	136 (0.5% sol.)	34[c]	1200	1250	18	26	28	13
5	5-6 days (2% sol.) 22 min. (0.1% sol.)	77[b]	500	550	15	12.5	15	6
6	5-6 days (2% sol.) 1-2 days (1% sol.) 19 min. (0.1% sol.)	21[b]	600	700	16	20	22.5	13
7	51 (2% sol.)	..	1600	1700	23	25	30	10
8	29 (2% sol.)	..	200	250	18	15	17.5	12
9	0	..	900	1000	17	45	50	10

[a] Not determined because of scarcity of material. [b] The dose in each of these cases was 0.1 cc. of a 1% solution. [c] The dose in this case was 0.1 cc. of a 0.5% solution.

pharmacological behavior of β-4-methylpiperidino-ethyl benzoate (1) with the isomeric 2- and 3-methyl derivatives shows a striking and unexpected difference. These latter compounds are without any apparent action on the rabbit's cornea,[1] but it is seen that (1) possesses considerable of such anesthetic action, nearly as much, in fact, as its propyl homolog.

Those compounds, (3), (4), (5), (6) and (7), that contain a phenyl-alkyl group are unusually effective in producing mucous membrane anesthesia, the anesthesia resulting from an application of a 2% solution lasting in some cases for five to six days. The ordinary durations of anesthesia are produced by these compounds in quite dilute solutions (0.1%). It should be noted that when a phenylethyl group is in the 4-position of the piperidine nucleus (Compound 7) the anesthetic action is considerably less than when a benzyl or phenylethyl group substitutes the 2-position of the piperidine nucleus. This suggests the possibility of an optimum position of the phenyl group relative to the nitrogen atom, for in the 2-benzylpiperidinopropyl benzoate (3) and the 2-phenylethylpiperidino-alkyl benzoates (4, 5 and 6) the phenyl group is separated from the nitrogen atom by 2 and 3 carbon atoms, respectively, *i.* e., the nuclei of phenylethyl and phenylpropyl groups are present in the anesthetic molecules, while in the case of the 4-phenylethylpiperidino-ethylbenzoate (7) the phenyl group is separated from the nitrogen atom by five carbon atoms, *i.* e., the nucleus of a phenylpentyl group exists. It is expected that some work now under way in this Laboratory will evaluate this possible relationship of structure to pharmacological action.

It is interesting to note that Compounds 5 and 6, which appear to be geometric isomers, show a difference in their pharmacological properties as well as in their physical properties. As nearly as can be judged they show about the same effect on the rabbit's cornea, but the durations of anesthesia produced by intracutaneous injection into the guinea pig and the subcutaneous and intravenous toxicities are markedly different. It should be noted that the less stable isomer (*i. e.*, the lower-melting one) is the more active physiologically.

Summary

1. A method for the isolation of y-picoline from coal tar bases has been described.
2. A number of new substituted piperidino-alkyl benzoates have been prepared.
3. All of these substances are local anesthetics. Certain of the phenylalkyl substituted derivatives are unusually potent anesthetics, producing anesthesia of the rabbit's cornea for a period of five to six days.
4. Some relationships between structure and pharmacological action are discussed.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

COMPARATIVE REACTIVITIES OF SOME SUBSTITUTED BENZYL HALIDES[1]

BY MURRAY M. SPRUNG[2]

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The present investigation is a study of the influence of substitution in the aromatic nucleus upon the reactivity of the benzyl halides. The metathetical reaction which has been chosen for investigation is that which occurs between the benzyl halides and an alkali sulfite, a reaction which has been used considerably in organic chemistry since its early discovery by Strecker,[3] and which occurs with an easily measurable speed at ordinary temperatures. The products of the reaction are a benzyl sulfonate and an inorganic halide.

The results of previous investigations of the velocity of replacement of halogen in the benzyl halides are not entirely concordant. Concordancy, in fact, may hardly be expected at present, in view of the complexity of this sort of problem, an insufficient understanding, as yet, of the more fundamental physico-chemical relationships involved, and the present sparsity of accurate experimental data. For the sake of brevity,

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[1] Presented, in part, at the Minneapolis meeting of the American Chemical Society, September, 1929.

[2] National Research Fellow in Chemistry.

[3] Strecker, *Ann.*, 148, 90 (1868).

the results of previous researches have been condensed into the form of a table (Table I). The important relationships may here be noted at a glance. Only a few additional comments need be made in order to accentuate a few relationships which cannot be made evident in the table.

Slator and Twiss,[4] who studied the reaction between some benzyl chlorides and sodium thiosulfate, used iodine titrations to follow the course of their reaction. They later found—hat iodine reacted with alkyl thiosulfates, giving rise to sulfides and disulfides. In the interpretation of their results, they seem to take no account of this disturbance.

Conant, Kirner and Hussey[6] investigated the reactivity of a few benzyl chlorides as a part of a much more exhaustive study of the reactivity of alkyl halides. An increase in reactivity toward potassium iodide of three- to nine-fold was observed when a nuclear nitro group or chlorine atom was present. However, a surprisingly greater reactivity was noted when a nuclear bromine atom was introduced. Both the ortho and the para isomer (the meta compound was not studied) reacted some two to three hundred times as rapidly as benzyl chloride itself. (No explanation was advanced for this apparently anomalous behavior. In all the other reactions listed in Table I, differences in reactivity brought about by nuclear substitution never exceeded several fold.)

The most exhaustive of the researches listed is that of Olivier,[7] who subjected these compounds to hydrolyis by means of aqueous alcohol (and later by means of aqueous acetone). The general results of this work indicated that a substituent has the same effect upon a side-chain chlorine atom that it has upon a nuclear hydrogen atom. That is, in case the nuclear substituent was a meta orienting group (a group decreasing the velocity of substitution of a nuclear hydrogen) the speeds of hydrolysis of isomeric substituted benzyl chlorides were in the order meta, ortho, para. When ortho-para orienting groups (groups which increase the velocity of substitution of nuclear hydrogen) were present, the order of reactivity of isomers toward aqueous alcohol was para, ortho, meta. In the theoretical papers of Olivier, and of Olivier and Berger, the conclusions were reached that steric factors played no part in these reactions; but that the results, with the exception of those of the ortho-substituted compounds, might be explained by considerations based upon the theory of alternate polarity of carbon compounds.

It may readily be seen that at the present time no extremely safe generalization may be made. It may be noted, however, that in all these reactions

[4] Slator and Twiss, J. *Chem. Soc.*, **95**, 93 (1909).

[5] Price and Twiss, *ibid.*, 95, 1489 (1909); Twiss, *ibid.*, 105, 1672 (1914).

[6] Conant, Kirner and Hussey, THIS JOURNAL, 47,488 (1925).

[7] Olivier, *Rec. trav. chim.*, 41,301,646 (1922); 42,516,775 (1923); 45,296 (1926); Olivier and Berger, *ibid.*, 45, 452 (1926); 46, 609, 861 (1927); Olivier, ***ibid.***, **48**, 227 (1929).

TABLE I

COMPARATIVE REACTIVITIES OF THE BENZYL HALIDES

Halides	Reagent	Nuclear substituent	Order of reactivity (un = unsub. halide)
Chlorides	Sodium thiosulfate in aqueous alcohol[4,5]	NO_2	*p*>*m*>*o*=un
Bromides	Aqueous alcohol8	OCH_3	*p*>*o*>un>*m*
		CH_3	*p*>*o*>*m*>un
		F	*p*>un>*o*>*m*
		Cl	un>*p*>*o*>*m*
		Br	un>*p*>*o*>*m*
		COOH	un>*m*>*p*
Bromides	HI in alcohol[S] .	OCH_3	*m*>un>*o*>*p*
		CH_3	*m*>*o*>*p*>un
		F	*o*>*m*>un>*p*
		Cl	un>*p*>*o*>*m*
		Br	un>*p*>*o*>*m*
		COOH	un>*p*>*m*
Chlorides	Sodium ethylate in absolute alcohol8	CH_3	*o*>*p*>*m*>un
		Cl	*p*>*m*>*o*>un
		Br	*m*>un>o
Chlorides	KI in acetones	NO_2	*o*>*p*>*m*>un
		Cl	*o*>*p*>un
		Br	*o*>*p*>un
Chlorides	Aqueous alcohol7 (and aqueous acetone)	CH_3	*p*>*o*>*m*>un
		NO_2	un>*m*>*o*>*p*
		Cl	un>*p*>*o*>m
		Br	un>*p*>o>m
		I	un>*p*>*o*>*m*
		COOH	un>*m*>*p*

except that of reduction with hydriodic acid,[8] ortho and para compounds were nearly always more reactive than the corresponding meta isomers. The ω-halogeno-toluic acids provided an exception to this order, and the nitrobenzyl chlorides in the case of the hydrolysis reaction of Olivier.[7] It should be mentioned that in the latter case the differences in reactivity of the isomeric nitro compounds were exceedingly small; the actual velocity constants at 83° were 0.0014, 0.0013 and 0.0011.

The present investigation was initiated primarily with the purpose of obtaining additional careful data. In this sort of work, theoretical deductions may most safely be made only when a large number of facts are available upon which to base these deductions.

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[8] Lapworth and Shoesmith, *J. Chem. Soc.*, 121, 1391 (1922); Shoesmith, *ibid.*, 123, 2828 (1923); Shoesmith, Hetherington and Slater, *ibid.*, 125, 1312 (1924); Shoesmith and Slater, ibid., 125, 2278 (1924); *ibid.*, 214 (1926); Shoesmith and Taylor, *ibid.*, 2832 (1926); Shoesmith and Connor, *ibid.*, 1768 (1927).

[9] Franzen, *J. prakt. Chem.*, [2] 97, 82 (1918); Franzen and Rosenberg, *ibid.*, [2] 101, 333 (1920).

Materials

Sodium sulfite crystals were obtained from Mallinckrodt. They were recrystallized twice from water and dried in an oven at 120°.

Benzyl chloride was obtained from Eastman. It was fractionated at atmospheric pressure and the fraction boiling at 178–179' was refractionated under vacuum. The fraction boiling at 81.5–82° at 28 mm. was used.

The following substances, obtained from the Eastman Kodak Company, were purified by fractionation under vacuum: o-chlorobenzyl chloride, b. p. 105–107° at 28 mm.; *p*-chlorobenzyl chloride, b. p. 113–115" at 24 mm.; o-bromobenzyl chloride, b. p. 117–119' at 21 mm.; o-chlorobenzyl bromide, b. p. 118–119° at 19 mm.

The following substances, obtained from Eastman, were purified by crystallization, as shown: *p*-bromobenzyl chloride, from 95% alcohol and from petroleum ether, m. p. 47.5–48°; *p*-nitrobenzyl chloride, three times from petroleum ether, m. p. 73.5–74.5°; *p*-chlorobenzyl bromide, twice from alcohol, m. p. 50.5–51.5°; *p*-nitrobenzyl bromide, twice from a mixture of alcohol and petroleum ether, m. p. 98.5–99°; o-nitrobenzyl chloride was obtained from Eimer and Amend. It was recrystallized from alcohol and from a mixture of alcohol and petroleum ether; m. p. 48.7–49.2°.

m-Bromobenzyl Bromide.—*m*-Bromobenzoic acid was reduced electrolytically, according to the method of Mettler.[10] The m-bromobenzyl alcohol thus obtained was treated with one molar equivalent of phosphorus tribromide. The bromide obtained boiled at 112–114° at 6 mm. It was recrystallized from a mixture of petroleum ether and alcohol; m. p. 42–42.4°.

***m*-Bromobenzyl Chloride.**—From m-bromobenzyl alcohol and thionyl chloride; purified by vacuum fractionation; b. p. 120–122° at 18 mm.

m-Chlorobenzyl Bromide.—The alcohol was obtained in 89% yield by electrolytic reduction according to Mettler.[10] From it the bromide was obtained in 83% yield by the action of one molecular equivalent of phosphorus tribromide. It was purified by vacuum fractionation; b. p. 110–111° at 12 mm.

***m*-Chlorobenzyl Chloride.**—From the alcohol in 78% yield by treatment with thionyl chloride; purified by vacuum fractionation; b. p. 111–113° at 25 mm.

o-Nitrobenzyl Bromide.—Twenty-five grams of o-nitrobenzaldehyde was converted to the alcohol by 15 g. of potassium hydroxide in 75 g. of water. The alcohol was treated with phosphorus tribromide, giving 60% of the theoretical quantity of the bromide, calculated on the basis of the aldehyde used. The bromide was recrystallized from alcohol, from a mixture of alcohol and petroleum ether, and from petroleum ether; m. p. 45.8–46.3°.

***m*-Nitrobenzyl Bromide.**—The alcohol was obtained by running a Cannizzaro reaction on m-nitrobenzaldehyde, and was converted to the bromide by phosphorus tribromide; b. p. 162–163" at 13 mm. It was then recrystallized from petroleum ether containing alcohol; m. p. 57° (sharp).

***m*-Nitrobenzyl Chloride.**—Ten and five-tenths grams of m-nitrobenzyl alcohol (obtained as above) gave 10.5 g. of m-nitrobenzyl chloride when treated dropwise with thionyl chloride; b. p. 173–174" at 34 mm. It was recrystallized from petroleum ether containing a little alcohol; m. p. 45.5–46.5°.

Method

The present experiments have been carried out in 50% (by weight) aqueous alcohol. Volumetric flasks were used for reaction vessels. The reactions were started by rapidly adding a known volume of a solution

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[10] Mettler, Ber., 38, 1749 (1905).

of sodium sulfite in 50% alcohol to a weighed quantity of the organic halide.[11] At desired intervals aliquot portions were withdrawn by means of calibrated, fast-flowing pipets. In the case of the benzyl bromides, these portions were run into excess standard iodine solution and the excess iodine titrated with standard thiosulfate. Parallel runs were made upon benzyl bromide, using two different methods, as follows: in the first of these the above procedure was followed; in the second case the withdrawn samples were simply run into cold water and the titrations were then rapidly accomplished, using standard iodine solution directly. The velocity constants thus obtained (5.86 and 6.12) checked within about 4%. It is therefore evident that in the case of the benzyl chlorides, where the mean reaction speeds are about forty times smaller than those of the benzyl bromides, there is no appreciable error involved in the second method of measurement. All subsequent runs upon the benzyl chlorides were, therefore, carried out according to this procedure, wherein the withdrawn samples were run into cold water and the unused sulfite was titrated rapidly with standard iodine solution.

The reactions follow the bimolecular law within experimental error (considered to be 5–8%). Bimolecular velocity constants were calculated on the basis of the time of mixing as zero time, unless the organic halide did not dissolve rapidly; the zero time was then taken as the time of the first withdrawal of a sample after true homogeneity was attained.

Preliminary Experiments Relative to the Reaction Mechanism

Qualitative Estimation of Sulfonate Formed.—That the products formed by the action of sodium sulfite upon various benzyl chlorides and bromides are actually the corresponding sodium sulfonates has been demonstrated by Clutterbuck and Cohen.[12]

Several of these experiments were repeated, and it was ascertained

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[11] Prepared solutions of the organic halide were not used, in order to minimize any hydrolysis or alcoholysis which might occur through the interaction of the organic compound and the mixed solvent. A small amount of alcoholysis or hydrolysis must necessarily occur during the reaction, but this factor is known to be entirely negligible in its influence upon the present results from the fact that the velocity constant of the hydrolysis of benzyl chloride by 50% alcohol [Olivier, *Rec. trav. chim.*, **41**, 301 (1922)] is nearly 1000 times smaller than the velocity constant found for the above replacement reaction. Direct experiments which confirmed this are described in a later part of this paper.

[12] Clutterbuck and Cohen, *J. Chem. Soc.*, **123**, 2507 (1923). For other applications of the Strecker reaction to benzyl compounds, see Eugene Fischer, German patent 48,722, *Friedlander*, **2**, 98 (1888); Marckwald and Frahne, *Ber.*, **31**, 1855 (1898); Böhler, *Ann.*, **154**, 51 (1870); Dahl and Company, German patent 55,138, *Friedländer*, 2, 386 (1889); Mohr, *Ann.*, **221**, 216 (1884); Weiss and Reiter, *ibid.*, **355**, 177 (1907); Bonomi da Monte and Zoso, *Gazz. chim. ital.*, **27**, II, 469 (1897); Purgotti and Monti, *ibid.*, **30**, II, 247 (1900); Purgotti and Lunini, *ibid.*, **33**, II, 334 (1903).

that 80–90% yields of benzyl sulfonates could be obtained by the usual methods of separation.

Oxidizing Action Due to the Organic Halide.—In the case of some alkyl halides the reaction with alkali sulfites leads to a certain amount of reduction to hydrocarbons and the formation of the corresponding quantity of sulfate. To see to what extent the present reaction was complicated by this factor, the sulfate present in 25 cc. of the sulfite solution at the beginning of a reaction with benzyl chloride and that present in 25 cc. of the reaction mixture after the reaction had run for six hours were precipitated as barium sulfate, with the following results.

Detectable in the unused solution, 0.1074 and 0.1045 g. of $BaSO_4$.

Detectable in the used solution, 0.1038 and 0.1044 g. of $BaSO_4$. Any oxidation due to the organic compound or due to air (auto-oxidation of the sulfite solution certainly does occur to some extent) is therefore of negligible consequence.

Auto-oxidation of the Sulfite Solution.—The amount of this occurring during an actual run has just been shown to be negligible. However, a slight amount does take place, as is shown by the following data. Twenty-five-cc. portions of different sulfite solutions were titrated with iodine before the start of a reaction, and again several hours later.

Initial iodine titer, cc.	33.87	35.90	43.20
Final iodine titer, cc.	33.51	35.40	42.90
Time elapsed, hours	6	8	9

The error due to this change was minimized by determining the initial iodine titer immediately before each run was started.

Extent of Hydrolysis and Alcoholysis.—Parallel runs were made in which the course of the reaction was followed on the one hand by iodine titration and on the other by titrations with hydrochloric acid in the presence of methyl red as indicator. Any formation of strong acid, due to either of the above reactions, should be evidenced by an increase in the ratio of iodine to hydrochloric acid required by equal amounts of the reaction mixtures at equivalent times. This ratio actually remained constant within titration error during the first 80% of the reaction. During the last 20% it increased somewhat. Two or three per cent. of strong acid (estimated on the basis of the initial reactants) was present after seventy hours, when the reaction was virtually complete.

Variation of the Velocity Constant with the Initial Concentration of the Reactants.—Experiments were made with benzyl chloride to determine the effect of variations in the initial concentrations of the reacting substances, and also to ascertain the effect of varying the ratio of the concentration of sulfite to benzyl halide. A summary of these results is given in Table II. There was a considerable range over which the velocity constant did not vary except within the experimental error (5–8%). At higher concentrations, however, there was noted a decrease in the velocity constant; and at very low initial concentrations the values increased markedly. When the initial concentrations were about 18 X 10^{-3} mole per liter, the normal value of 0.391 had increased to 0.430, and had further increased to 0.536 when the initial concentrations were 12.7 X 10^{-3} mole per liter. From Table II it is also evident that the velocity constant depends about as much upon the initial concentration of one reactant as upon the other. Thus, when the initial concentration of either reactant was about 12.5 X 10^{-3}, while that of the other was within the "normal range," that is, about 24 X 10^{-3}, the calculated constants also fell within the normal range. It is certain that the variations are no greater than 8% when the concentrations of both reactants lie between 40 X 10^{-3} and 20 X 10^{-3} mole per liter. Therefore, in all runs made for the determination of comparative reactivities, the initial concentrations of both reacting substances were taken so as to be well within this range, and the values obtained are, therefore, strictly comparable within the general limit of accuracy permitted by the experimental technique employed.

TABLE II

VARIATION OF THE VELOCITY CONSTANT WITH THE INITIAL CONCENTRATION OF THE REACTANTS

A, concn. of benzyl chloride (moles/liter). B, concn. of sodium sulfite (moles/liter). Temp., 40.00 ± 0.03°

No.	A X 10^{-3}	B X 10^{-3}	K_{mean} (bimol.)
1	903	45.2	0.320
2	62.0	28.1	.388
3	57 5	28 1	.381
4	40 9	40 3	.398
5	332	33.7	.386
6	331	333	.408
7	29 9	29 9	381
8	274	268	.397
9	22.8	23.4	0.376
10	20.4	34.2	.395
11	23.8	12.12	.408
12	12.56	24.20	.396
13	18.24	18.24	.430
14	12 70	12.70	.536
15	11.48	8.72	.615

Average of 2–12, 0.392.

The Effect of Variations in *PH*.—Parallel experiments were carried out with benzyl chloride in which the PH of the solution was varied by using sodium sulfite alone, sodium sulfite buffered by sodium acetate, and sodium bisulfite. The calculated velocity constants were 0.386, 0.370 and 0.006. When an equimolecular mixture of sodium sulfite and sodium bisulfite was used, the calculated "constants" decreased from 0.180 to 0.04 within a given run, as the reaction proceeded. It appears, therefore, that the reaction actually occurs between the organic halide and sulfite ion as follows: $RCH_2X + SO_3^{=} \longrightarrow RCH_2SO_3^{-} + X^{-}$. In the case of the sulfite–bisulfite mixture, the PH of the solution changes as the reaction proceeds, due to the reversible change of sulfite into bisulfite ions, and since there is available no real measure of the sulfite-ion concentration, no proper velocity constants may be calculated. In the case of the sulfite, the bisulfite or the sulfite–acetate, the PH of the solution must remain nearly constant, and, therefore, the concentration (or activity) of sulfite ion is proportional, within a few per cent., certainly, to the total concentration of the molecular species. In the case of sodium sulfite alone, the sulfite ion activity is probably, within a small error, equal to the total concentration of sodium sulfite molecules. (Any differentiation between "concentration" and "activity" is necessarily meaningless as far as the present results extend.)

Addition of sodium hydroxide to the reaction mixture causes the velocity "constants" to fall off rapidly within a run. This is undoubtedly due to side reactions which occur with appreciable speeds in an alkaline medium. These side reactions may be the formation of benzyl alcohol, or of stilbene, or both, since both reactions are known to occur to some extent in a medium of sufficient alkalinity.[13]

Discussion of the Results

A few typical experiments are reproduced in Table III. For the benzyl chlorides there is no noticeable drift in the values of the velocity constants during the first 75% of the reaction. The agreement within a given run is all that could be expected. For the benzyl bromides, where the reaction speeds are about forty times faster, the velocity constants show no perceptible drift during the first 90% of the reaction. In all cases the mean values were reproducible to within 8% and usually to within 4–5%.

TABLE III

TYPICAL DATA CONCERNING THE REACTION BETWEEN SOME BENZYL HALIDES AND SODIUM SULFITE IN 50% AQUEOUS ALCOHOL

Benzyl chloride at 40.00 ± 0.03°

Benzyl chloride, 0.04088 *M;* sodium sulfite, 0.04032 *M;* titrations (25 cc.) with 0.02316 M iodine

Time, minutes	Iodine, cc.	*K* (bimol.)
0.0	43.55	...
30.5	28.97	0.403
59.5	21.94	.403
105.5	15.83	.400
165.5	11.85	.388
255.5	8.24	.398
	Av.	.398

o-Chlorobenzyl chloride at 40.00 ± 0.03°

o-Chlorobenzyl chloride, 0.02936 *M;* sodium sulfite, 0.02920 M; titrations (25 cc.) with 0.02300 M iodine

Time, minutes	Iodine, cc.	K (bimol.)
0.0	31.84	...
15.0	27.77	0.333
35.5	23.78	.328
70	19.17	.325
120	14.98	.323
140	13.86	.319
210	10.71	.323
330	7.42	.338
	Av.	.328

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[13] Shoesmith and Slater, *J. Chem. Soc.*, 125, 2287 (1924); Acree, *Am. Chem. J.*, 29, 593 (1903); Tschitschibabin, *Chem. Zentr.*, I, 1301 (1902); Staudinger and Kupfer, *Ber.*, 44, 2194 (1911); Bergmann and Hervey, *ibid.*, 62, 900 (1929).

TABLE III (*Concluded*)

m-Chlorobenzyl bromide at 30.00 ± 0.03°

m-Chlorobenzyl bromide, 0.03020 *M;* sodium sulfite, 0.03020 *M;* titrations (25 cc.) with 0.02231 *M* iodine and 0.03452 M $Na_2S_2O_3$

Time, minutes	Iodine, cc.	$Na_2S_2O_3$ cc.	K
0	39.97	7.88	..
4.5	26.57	3.00	2.94
10	19.98	2.20	2.84
15	20.17	7.48	3.00
25	15.01	6.26	3.08
35	15.10	9.26	3.08
50	15.05	11.05	2.96
70	14.95	13.37	3.04
		Av.	3.00

o-Nitrobenzyl bromide at 30.00 ± 0.03°

o-Nitrobenzyl bromide, 0.03530 *M;* sodium sulfite, 0.03530 *M;* titrations (37.5 cc.) with 0.02231 *M* iodine and 0.03452 *M* $Na_2S_2O_3$

Time, minutes	Iodine, cc.	$Na_2S_2O_3$, cc.	K
0	59.10	0.00	...
3	39.87	1.76	10.13
7	31.14	6.40	10.20
12	19.97	2.30	10.60
20	15.07	3.34	10.53
30	15.04	7.83	10.60
45	15.06	11.54	10.81
		Av.	10.48

The average velocity constants at 40° for the benzyl chlorides are summarized in Table IV. Prom this it may be seen that a nuclear nitro group increases the reactivity of the halide toward sodium sulfite regardless of its position. The greatest effect is produced when the nitro group is present in the para position, and the smallest effect when it is introduced into the meta position. A nuclear chloro or bromo atom causes a decrease in the reactivity toward sulfite ions in every case except that of the *p*-bromo compound.[14] In both cases the para isomer is the most reactive, the ortho isomer next, and the meta isomer has the lowest reactivity. The order is thus the same as that found in the case of the nitro derivatives. The results obtained when working with the benzyl bromides are summarized in Table V. The bromides conform to the same general relationships as the chlorides. A nuclear chlorine atom decreases the rate of replacement, whereas a nitro group increases the reactivity in this reaction. In both cases the relative reactivities of a group of isomers is para > ortho > meta, parallel with that of the benzyl chlorides. m-Bromobenzyl bromide is less reactive than benzyl bromide. (In this case the ortho and para isomers were not investigated.) The reaction velocities of the halogen compounds are in the same order at 40° as at 30°. The temperature coefficients vary, however, from 1.90 for the m-bromo compound to 3.18 for benzyl bromide itself.

The present results are in agreement with the generalization previously

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[14] This is an anomalous effect for which there is, at present, no adequate explanation. The actual value of the velocity constant, however, was carefully checked. Two separate runs upon a product which had been purified by crystallization first from alcohol and then from petroleum ether gave values of 0.453 and 0.468. The substance was then recrystallized from alcohol and from benzene. The melting point was raised half a degree by this procedure. The average value of the velocity constant obtained when using the repurified substance was, however, 0.477, or within 4% of the previous average.

TABLE IV

RELATIVE REACTION RATES OF BENZYL CHLORIDES WITH SODIUM SULFITE (TEMP., 40.00 ± 0.03°)

Benzyl chloride cpd.	K_{mean} (bimol.)
Benzyl chloride	0.392
p-Chloro-	0.345
o-Chloro-	.328
m-Chloro-	.238
p-Bromo-	.465
o-Bromo-	.262
m-Bromo-	.238
p-Nitro-	.738
o-Nitro-	.525
m-Nitro-	.487

For benzyl chloride at 30.00°, $K = 0.169$. Temp. coeff., 2.32.

TABLE V

RELATIVE REACTION RATES OF BENZYL BROMIDES WITH SODIUM SULFITE

Compound	40.00 ± 0.03° K_{mean} (bimol.)	30.00 ± 0.03° K_{mean} (bimol.)	Temp. coeff.
Benzyl Bromide	5.86	18.6	3.18
p-Chloro-	5.17	14.2	2.75
o-Chloro-	3.84	8.67	2.26
m-Chloro-	3.00	7.16	2.38
m-Bromo-	3.40	6.42	1.90
p-Nitro-	17.2		
o-Nitro-	10.5		
m-Nitro-	9.55		

made, on the basis of a résumé of the previously existing literature, that in nuclear substituted benzyl halides ortho and para isomers usually show a greater reactivity toward replacement reagents than the corresponding meta isomer. The consistency of the relative order of reactivity of isomers (para > ortho > meta) found for this replacement reaction was, however, not to be anticipated.

Summary

1. A kinetic study has been made of the replacement reaction between some substituted benzyl halides and sodium sulfite in 50% aqueous alcoholic solution. The reactions are bimolecular. In the case of benzyl chloride the calculated velocity constants increased as the initial concentrations of the reactants were decreased.

2. The introduction of a nuclear nitro group into benzyl chloride or bromide increased the speed of this reaction, regardless of position. A nuclear chlorine or bromine atom decreased the speed of the reaction, except in the case of *p*-bromobenzyl chloride. This compound reacted considerably faster than benzyl chloride.

3. The order of reactivity of isomers was in all cases, para > ortho > meta.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

COMPARATIVE REACTIVITIES OF SOME CHLORO- AND BROMONITROBENZENES[1]

BY MURRAY M. SPRUNG[2]

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The nitrophenyl halides react with alkali sulfites in alcoholic or aqueous alcoholic solution to give nitrophenyl sulfonates.[3]

In the expectation that this reaction would furnish another means for quantitative study of the nitrophenyl halides, and in the hope of obtaining some additional information relating to the mechanism of activation of groups in aromatic compounds, the velocity measurements reported in the preceding paper have been extended to some of these more reactive nuclear halogen compounds.

Practically all of the previous data concerning the reactivity of aromatic halogen have been obtained by using as reagents either amines[4] or alcoholates.[5] Rheinlander,[4d] using aniline and monomethylaniline as reagents, found that the ratio between the reactivity of a 2,4-dinitro-halogeno-benzene and the corresponding symmetrical trinitrophenyl halide was approximately 1:7. Brewin and Turner,[4e] using pyridine in boiling benzene, found a surprising difference in reactivity between an ortho and para mononitro halide; but they also found that the introduction of a second nitro group did not materially increase the reactivity. Thus the ratio of the reactivities of the nitrochloro compounds was para:ortho:2,4-dinitro = 1:36.3:56.9. For the corresponding bromo compounds the ratio was 2.38:43.5:56.4, while the iodo ratio was 2.24:17.9:34.4.

The Dutch school, led by Lobry de Bruyn, Lulofs, and Holleman, has

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[1] Presented, in part, at the Minneapolis meeting of the American Chemical Society, September, 1929.

[2] National Research Fellow in Chemistry.

[3] E. and H. Erdmann, German patent 65,240, *Friedländer*, 3, 41 (1891); *Ann.*, 294, 380 (1897); Willgerodt, *J. prakt. Chem.*, [2] 32, 117 (1885); Willgerodt and Mohr, *ibid.*, [2] 34, 118 (1886); Geigy and Company, German patent 94,504, *Friedlander*, 4, 188 (1897); German patent, 88,952, *Friedlander*, 4, 133 (1896); Purgotti and Lunini, *Gazz. chim. ital.*, 33, II, 334 (1903).

[4] (a) De Mooy, *Rec. trav. chim.*, 35, 5 (1915); (b) Ter Weel, *ibid.*, 35, 44 (1915); (c) Franzen and Bockhacker, *Ber.*, 53, 1174 (1920); (d) Rheinlander, *J. Chem. Soc.*, 123, 3099 (1923); (e) Brewin and Turner, *ibid.*, 332,334 (1928).

[5] Lobry de Bruyn, *Rec. trav. chim.*, 9, 197 (1890); Lowenherz, *Z. physik. Chem.*, 29, 401 (1899); 36, 469 (1901); Lulofs, *Rec. trav. chim.*, 20, 292 (1901); Brand, *J. prakt. Chem.*, [2] 67, 145 (1903); Beekmann, *Rec. trav. chim.*, 23, 254 (1904); De Mooy, *ibid.*, 35, 5 (1915); Ter Weel, *ibid.*, 35, 44 (1915); Holleman, *ibid.*, 37, 195 (1917); 39, 736 (1920); den Hollander, *ibid.*, 39, 436 (1920); Holleman and van Haeften, *ibid.*, 40, 67 (1921); Mattaar, *ibid.*, 41, 103 (1922); Van de Vliet, *ibid.*, 43, 620 (1924); Baudet, *ibid.*, 43,718 (1924); Van der Kam, *ibid.*, 45, 564 (1926); Lorang, *ibid.*, 46, 891 (1927); Talen, *ibid.*, 47, 329 (1928).

been particularly interested in determining which group of a phenyl compound highly substituted by both nitro and chloro groups would be replaced, and from which position it would be replaced. Working mainly with sodium methylate or ethylate, they have amassed much valuable information of this kind. The conclusions in which we are most interested at present are these: a chlorine atom ortho or para to one or more nitro groups will usually be replaced; in some cases a nitro group ortho or para to one or more other nitro groups may be replaced; a para nitro group usually has considerably more mobilizing influence than an ortho nitro group; a halogen atom, especially when in the meta position, may to some degree activate a second halogen atom or a nitro group. Di and tri meta compounds were shown to be in all cases decidedly unreactive. In general, a trinitro-chloro compound was about thirty times more reactive than a dinitro-chloro compound. The 2,4,6-trinitro halides were stated to be "very reactive."

In both of the above series of researches (with amines and with alcoholates) there was no general agreement as to the relative replaceability of halogen atoms in analogous compounds. In many cases bromine atoms were replaced more readily than chlorine, but frequently just the reverse was true.

Materials

The following compounds were obtained from Eastman and purified as given: picryl chloride was recrystallized twice from ethyl alcohol–benzene mixture, m. p. 81.5–82.5°; 2,4-dinitrochlorobenzene was recrystallized three times from alcohol, m. p. 50.5–50.6°; o-nitrochlorobenzene was recrystallized three times from alcohol, m. p. 32.0–32.6°; m-nitrochlorobenzene was recrystallized from alcohol, m. p. 44–45°; p-nitrochlorobenzene was recrystallized three times from alcohol, m. p. 82.5–83.5°; o-nitrobromobenzene (m. p. 42.5–43°), m-nitrobromobenzene (m. p. 55–55.5°), *p*-nitrobromobenzene (m. p. 126.5–127°) and 2,4-dinitrobromobenzene (m. p. 72–72.5°) were available in a pure state.

Method

The present experiments were carried out using the method described in the preceding paper. Because of the slow solubility of the nitro halides in 50% alcohol, the reactions were not started by adding the sulfite solution to the pure halide. Instead, a solution of the halide in 50% alcohol was made up to a definite volume just prior to use, and an equal volume of the sulfite solution was rapidly added to this. In the case of the mononitro compounds the progress of the reaction was followed by running portions into cold water and titrating the unused sulfite directly with iodine. In the case of the more reactive di- and trinitro compounds, the reactions were stopped by running the solutions into excess iodine and titrating the excess with standard thiosulfate.

Discussion of the Results

Two typical runs are shown in Table I, and the complete results are assembled in Table II. The accuracy of the results in respect to the dinitro compounds is considered to be about 5%, which is the general accuracy of the results obtained with the benzyl bromides. The average velocity constants found for the mononitro halides are of the order of 0.010, and are considered to be subject to an error of ±0.002. The value for picryl chloride (160) is probably correct to within 20%.

TABLE I

TYPICAL DATA CONCERNING THE REACTION BETWEEN SOME NITROPHENYL HALIDES AND SODIUM SULFITE IN 50% AQUEOUS ALCOHOL

o-Nitrochlorobenzene at 40.00° o-Nitrochlorobenzene, 0.02176 *M;* sodium sulfite, 0.02176 *M;* titration (50 cc.) with 0.02686 *M* iodine

Time. minutes	Iodine, cc.	K_{mean} (bimol.)
0	40.4	....
15	40.3	0.0084
45	40.1	.0075
105	39.7	.0077
225	39.05	.0071
475	38.2	.0070
465	37.5	.0076
	Av.	.0075

2,4-Dinitrobromobenzene at 40.00' **2,4-Dinitrobromobenzene,** 0.02390 *M;* sodium sulfite, 0.02390 *M;* titration (50 cc.) with 0.02686 M iodine and 0.03888 *M* $Na_2S_2O_3$

Time. minutes	Iodine (net), cc.	K_{mean} (bimol.)
0	42.5	....
2	21.7	18.5
5	11.8	18.7
9	6.8	18.8
14	4.1	18.6
21	2.3	18.7
30	1.2	18.5
	Av.	18.6

TABLE II

RELATIVE REACTIVITIES OF NITROCHLORO- AND NITROBROMOBENZENES TOWARD SODIUM SULFITE

Compound	Temp., 30.00' K_{mean} (bimol.)	Temp., 40.00° K_{mean} (bimol.)	Temp. coeff.
p-Nitrochlorobenzene[a]	0.003	0.006	Approx. 2
o-Nitrochlorobenzene[a]	.004	.008	Approx. 2
m-Nitrochlorobenzene[a]	.005	.011	Approx. 2
p-Nitrobromobenzene[a]	....	.016	....
o-Nitrobromobenzene[a]	....	.006	....
m-Nitrobromobenzene[a]	....	.008	....
2,4-Dinitrochlorobenzene[b]	6.14	10.25	1.67
2,4-Dinitrobromobenzene[c]	....	18.6	....
2,4,6-Trinitrochlorobenzene[d]	160	Immeasurably fast	

[a] At the end of each reaction (or, in the cases of the very slow ones, after the reaction had proceeded for several hours) the solutions were tested qualitatively for chloride, nitrite, and for the presence of reduced nitrogen compounds. The latter test was carried out as follows: a portion of the solution was boiled with strong sulfuric acid, then cooled, and made alkaline with sodium hydroxide. A few cc. of chloroform was added and the solution boiled. No carbylamine odor was detectable in any case, showing that no amines or sulfamic acids or similar reduced nitrogen compounds which could be hydrolyzed to amines were formed. Nitrite ion could be detected in none of the reaction mixtures. A positive test for chloride ion was obtained in each case.

[b] When the reactants were mixed, a pink color developed. The color faded as the reaction proceeded and had turned to a pale yellow when the reaction was approximately 60% complete. This change is due, in all probability, to the indicator action of 2,4-dinitrophenylsulfonic acid, the reaction product (see footnote d).

[c] A similar pink color was produced here. It had turned to a pale yellow when the reaction was approximately 60% complete.

[d] A deep red color formed upon mixing the reactants and faded gradually as the reaction proceeded, finally attaining a yellow-green shade. This color change is due, undoubtedly, to the fact that *sym.*-trinitrophenylsulfonic acid is an indicator of the same type as *sym.*-trinitrobenzene. The color reactions of trinitrobenzene which lead to its use as an acidimetric indicator are usually attributed to the ability of this compound to take on addenda of various sorts. The addition products are stable in alkaline solution, but usually break down into their constituents in solutions of a lower PH. (Trinitrobenzene changes color at a PH of about 12.) The addition products have been formulated as quinonoid complexes [Hantzsch, *Ber.*, 42,2120 (1909)] and as secondary valency complexes. [See, for example, Sudborough and Beard, *J. Chem. Soc.*, 97, 780 (1910); Sudborough, *ibid.*, 109, 1339 (1916); Pfeiffer, *Z. anorg.* Chem., 137, 287 (1924).] The change from the "alkaline" to the "acid" color during the course of the present reaction is probably due to the fact that as the reaction proceeds sodium sulfite is used up and sodium trinitrophenyl sulfonate is formed. Since trinitrophenyl sulfonic acid is undoubtedly a stronger acid than sulfurous acid, the PH of the solution decreases, eventually reaching the "neutrality" point, that is, the point where the red complex is completely dissociated into its components, the yellow "acid" color being due to the trinitrophenyl sulfonate ion.

From one of these experiments the sodium trinitrophenyl sulfonate was isolated (2.55 g. from 2.55 g. of the trinitrophenyl chloride) and its indicator action noted. It is a fairly good acidimetric indicator, havicg quite an abrupt change from red to yellow. It may be used in the titration of either strong or weak acids.

It is interesting to note that the reactivities of analogous bromine and chlorine derivatives are very close together, and that there is evidently no general rule as to which is more reactive. This is in accord with general experience with nuclear halogen. About as many pairs of compounds have been investigated in which the bromine compound has shown a greater reactivity than the chlorine compound as of those in which the reverse relationship has been found to hold.

The mononitrochlorobenzenes reacted, at 30°, at a rate which was just measurable by means of the present experimental technique. The velocity constants for the ortho, meta and para isomers differ by less than the experimental error. However, all three compounds were run at the same time and under exactly parallel conditions, so that it is certain that the relative reactivities are in the order given, that is, meta > ortho > para. The same relative order holds also at 40°. In the mononitrobromo series, the order at 40° is para > meta > ortho, the para isomer reacting over twice as fast as either of the other two. Here again one may be sure of the relative order by virtue of the fact that the three compounds were run under as nearly as possible identical conditions. From the fact that the meta compounds show the same order of reactivity as their ortho and para isomerides, it seems that in the reaction of the mononitrophenyl halides with sulfite the activation of the halogen atom by the nitro group must be due to its specific polar influence, and not to its ability to induce any sort of alternating effect within the benzene ring.

In this reaction the 2,4-dinitrophenyl halides were found to be approximately two thousand times as reactive as the mononitrophenyl halides, a result which is in marked contrast to those obtained by Brewin and Turner,[4e] who found that the introduction of a second nitro group did not materially alter the reactivity of a mononitrophenyl halide toward pyridine. Picryl chloride, the only trinitrophenyl halide studied during the present investigation, was about *25* times more reactive than either of the dinitrophenyl halides, a result which is approximately in agreement with those of Rheinlander,[4d] and also with those of the Dutch chemists.[5] None of these latter investigators compared the reactivities of the mono and dinitro halides. However, some of the qualitative results of the Dutch school[4"] indicate that the ratio of reactivities of tri- and dinitro halides toward alcoholates would be of the order of magnitude of 10^3, and therefore in agreement with the present results.

It is significant that the large increase in activating power occurs upon the introduction of the second nitro group, while the third nitro group has comparatively small influence. The fact that the mononitro compounds show the same order of reactivity irrespective of the position of the nitro group should also be emphasized, for it is well known, in regard to dinitrophenyl compounds, that two nitro groups in the meta positions with respect to a third group affect the reactivity of this group remarkably less than two nitro groups in the ortho and para positions with respect to the third group. A similar feeble activating influence of a single meta nitro group, relative to that of an ortho or para nitro group, might be expected, but is certainly not found in the present reaction.

Summary

1. The reaction between some nitrophenyl halides and sodium sulfite has been studied kinetically.

2. Toward this reagent, analogous chloro- and bromonitrophenyl halides show the same order of reactivity.

3. m-Nitrobromobenzene and *m*-nitrochlorobenzene react with approximately the same speeds as their ortho and para isomerides.

4. **A** 2,4-dinitrophenyl halide is about 2000 times more reactive than a mononitrophenyl halide. Picryl chloride is only about 25 times more reactive than 2,4-dinitrochlorobenzene.

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CONDENSATIONS OF SECONDARY AMINES WITH ALDEHYDES AND NAPHTHOLS1

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In a study of resolving agents for the preparation of optically active compounds, 1-(α-aminobenzyl)-2-naphthol[2,3] was prepared, as well as a number of substituted derivatives which will be described in a later paper. Betti in an earlier article[4] observed that secondary amines did not undergo this condensation with β-naphthol and benzaldehyde to form a compound similar to that formed by ammonia and primary amines. Betti's explanation for the condensation between β-naphthol, benzaldehyde and ammonia or a primary amine involved first the formation of a benzylidine-amine such as $C_6H_5CH{=}NR$, followed by addition between the double bond of this compound and the activated H in the a-position in @-naphthol. By such an explanation condensation with secondary amines is precluded.

In our experiments condensations with secondary amines, benzaldehyde and @-naphtholwere attempted and definite condensation products were isolated, particularly with dimethylamine, diethylamine and piperidine. These compounds are similar to the condensation products of the monoamines and ammonia and gave correct analyses for 1-(α-dimethylaminobenzyl)-2-naphthol, 1-(α-diethylaminobenzyl)-2-naphthol, and 1-(*a*-1-piperidylbenzyl)-2-naphthol.

Since the isolation of these compounds Dilthey and Stallman[5] have reported on the addition of aldehydes and secondary amines to active methylene compounds of the dibenzyl ketone type, which is undoubtedly capable of enolization into an enol form, —CH=C(OH)—, and which would be equivalent to the *a*- and β-groups in β-naphthol. This latter work confirms the possibility of the condensation of secondary amines with aldehydes and active methylene groups and necessitates a revision in the theory of Betti's condensations, which should also fit the theory of Dilthey and Stallman's reaction, as well as similar condensations such as Dimroth's[6] condensation of amides and phenols, Knoevenagel's reaction,[7] Claisen's acid condensation, Perkin's synthesis, etc. The same

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[1] An abstract of a portion of a thesis submitted by Joseph B. Littman in partial fulfilment of the requirements for the degree of Doctor of Philosophy at The Ohio State University.

[2] Betti, *Gazz.* chim. *ital.*, 31, *1, 385* (1901)

[3] "Organic Syntheses," John Wiley and Sons, Inc , New York, 1929, Vol. IX, p. 60.

[4] Betti, Gazz. *chim. ital.*, 30, II, 310 (1900).

[5] Dilthey and Stallman, *Ber.*, 62, 1603 (1929).

[6] Dimroth, *ibid.*, 35, 995 (1902)

[7] Knoevenagel, *ibid.*, 37, 4446 (1904).

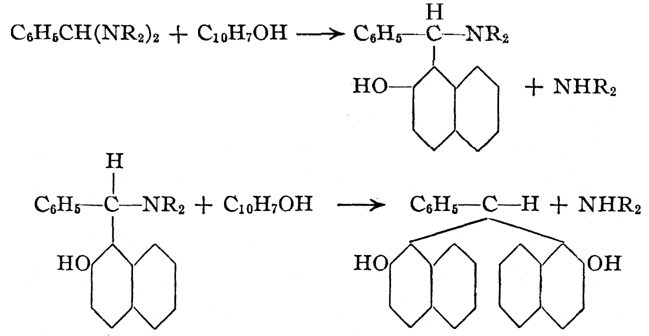
mechanism should hold in all cases where similar compounds are formed from similar reagents.

Dilthey and Stallman confirmed the structure of their condensation compound by treating $(C_6H_5CH_2)_2CO$ with benzylidene dipiperidine, with which they obtained the same compound as before, together with an equivalent amount of piperidine. Using this same reagent with β-naphthol, the condensation took place with the formation of the same compound that was obtained by the direct interaction of the three original materials. While this does not confirm the existence of benzylidene dipiperidine as an intermediate in the condensation, it furnishes additional data on the mechanism of the reaction.

The reaction of the amine with the aldehyde is admitted by Betti and others as the first step in the condensation, and after this addition or dehydration, the second condensation or addition of the naphthol, phenol or active methylene takes place.

In the case of secondary amines no such condensation with benzaldehyde can take place so as to form an imine type of condensation product; rather, a benzylidinediamine or hydroxyamine is formed which splits out a molecular equivalent of amine or water on its condensation with the active methylene.

$$C_6H_5CHO + 2HNR_2 \longrightarrow C_6H_5CH(NR_2)_2 + \mathrm{Hz0} \qquad (1)$$



(2)

(3)

The entire condensation is, of course, comparable with the Knoevenagel reaction, the Claisen condensation or other reactions between a carbonyl and active methylene.[8] Knoevenagel showed that amines catalyzed his condensations and he actually carried out the reaction with benzaldehyde, piperidine, and acetoacetic ester as his active methylene compound and explained his reaction in two steps, as above, first, the formation of the benzylidine dipiperidine compound and then, second, its reaction with the active hydrogens in acetoacetic ester to yield $C_6H_5CH = C\begin{matrix} \diagup COCH_3 \\ \diagdown COOC_2H_5 \end{matrix}$. He did not obtain or isolate the intermediate mono secondary amino

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[8] Knoevenagel, *Ann.*, 288, **321** (1895).

compound. Dilthey and Stallman have in their work carried out the reaction in a way so as to obtain the obvious intermediate product, which must undoubtedly yield on further heating or acid treatment the final product analogous to that obtained by Knoevenagel. Applying the same theory to the naphthol condensation, it is impossible to obtain a compound of the ethylene type since there is only one replaceable H in the a-position in β-naphthol, but with an excess of β-naphthol one should obtain the di-β-naphthol benzal compound, which can be made by direct interaction of benzaldehyde and β-naphthol,[9] and this was actually obtained by heating the dimethyl condensation compound with an excess of β-naphthol in benzene.

In the case of the piperidine condensation product, the melting point of the B-naphthol condensation product was practically the same as that of the above compound, but the latter contained no nitrogen and the mixed melting point of the two gave a depression of nearly 25°.

It is apparent in the above reactions, as well as in the work of Dilthey and Stallman, that we are dealing with possible intermediate products in the more or less standard reaction between a carbonyl and active methylene. The isolation of these intermediate products is best explained on the mild activity of the active methylene groups and the use of an excess of the amine. The use of an excess of the active methylene compound (β-naphthol in our reaction) produced as in the work of Knoevenagel and others the substitution of both of the valences of the carbinol with the methylene radical.

Experimental

Preparation of **1-(α-dimethylaminobenzyl)-2-naphthol.**—Ninety-six grams ($^2/_3$ mole) of β-naphthol was dissolved in a mixture of 70.6 g. ($^2/_3$ mole) of benzaldehyde and 100 cc. of 95% ethyl alcohol. Through this solution dimethylamine gas was passed, generated from 140 g. of a 33% methylamine–water solution by heating in a flask attached to a reflux condenser. The solution turned dark brown in color and became very warm. It was necessary to cool the flask with cold water. On standing for twenty-four hours in a tightly stoppered flask, fine white crystals formed which were filtered off and washed twice with small amounts of alcohol. The crude product melted at 148–160°. It was recrystallized thrice from a mixture of benzene and ligroin; m. p. 164–164.5°; yield, 130 g. or 70.7% of the theoretical. The compound is moderately soluble in benzene, slightly soluble in alcohol, and insoluble in water. When dissolved in benzene and treated with an ether solution of ferric chloride it gives an intense violet coloration. The alcohol solution gave a yellow color on heating, and became colorless on cooling.

Anal. Calcd. for $C_{19}H_{19}ON$: C, 82.3; H, 6.86; N, 5.1. Found: C, 81.83; H, 6.91; N, 5.18.

Hydrochloride of **1-(α-Dimethylaminobenzyl)-2-naphthol.**—Two grams of 1-(α-dimethylaminobenzyl)-2-naphthol was suspended in 125 cc. of water to which 5 cc. of concentrated hydrochloric acid was added. On warming the solution carefully

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[9] Hewitt and Turner, *Ber.*, 34, 202 (1901).

the compound went into solution, followed by the precipitation of the hydrochloride in very fine white crystals which were filtered off with suction, and washed a few times with water. The hydrochloride decomposed at 208–210°.

Anal. Calcd. for $C_{19}H_{20}ONCl$: Cl, 11.32. Found: Cl, 11.3%.

1-(α-1-Piperidylbenzyl)-2-naphthol.—Twenty-nine grams (0.2 mole) of 8-naphthol was dissolved in a mixture of 21 g. (0.2 mole) of benzaldehyde and 25 cc. of absolute alcohol. To this solution in a small flask, 17 g. (0.2 mole) of piperidine was slowly added, the flask corked and allowed to stand for forty-eight hours. A small amount of heat was evolved. The small white crystals were filtered off and washed twice with alcohol. The crude product melted from 178 to 196°. It was recrystallized thrice from a mixture of benzene and ligroin and melted at 198–198.5°; yield, 46 g., or 72.5% of the theoretical. This compound also gives a violet coloration with ferric chloride in ether–benzene solution and also gives in hot alcohol a yellow coloration which disappears on cooling.

Anal. Calcd. for $C_{22}H_{23}ON$: C, 83.28; H, 7.25. Found: C, 83.01; H, 7.32.

Hydrochloride of **1-(α-1-Piperidylbenzyl)-2-naphthol.**—Two grams of 1-(a-1-piperidylbenzyl)-2-naphthol was treated in the same manner as 1-(a-dimethylaminobenzyl)-2-naphthol. The hydrochloride separated as a fine white precipitate. It decomposed at 203–205°.

Anal. Calcd. for $C_{22}H_{24}ONCl$: Cl, 10.04. Found: Cl, 10.4.

Preparation of I-(a-Diethylaminobenzy1)-2-naphthol.—Thirtysix grams (0.25 mole) of β-naphthol and 27 g. (0.25 mole) of benzaldehyde were dissolved in 50 cc. of absolute alcohol. To this solution 28 g. (0.25 mole + 10 g. excess) of diethylamine was added and the solution became slightly warm. Considerable difficulty was experienced in getting the compound to crystallize out. After five weeks' standing crystals started to form. They were filtered and washed with alcohol. The crude product melted at 101–106°. Recrystallization from alcohol raised the melting point to 117–118°; yield, 15.5 g., or 20.8% of the theoretical. This compound, like the other two, gives a violet coloration with ferric chloride in benzene–ether solution and also gives a yellow coloration in hot alcohol, which disappears on cooling.

Anal. Catcd. for $C_{21}H_{23}ON$: N, 4.6. Pound: N, 4.64.

Preparation of **1-(α-1-Piperidylbenzyl)-2-naphthol** from 8-Naphthol and **Benzylidine Dipiperidine.**—Benzylidine dipiperidine was prepared according to the method of Laun.[10] Ten and four-tenths grams of benzylidine dipiperidine was dissolved in 75 cc. of 95% ethyl alcohol. To this solution 6 *g.* of 8-naphthol dissolved in 15 cc. of alcohol was added. After forty-eight hours the mixture yielded 3 g. of 1-(α-1-piperidylbenzyl)-2-naphthol. The crude product melted at 195–197°. Recrystallization from a mixture of benzene and ligroin gave a melting point of 197–198°. A mixed melting point with the 1-(α-1-piperidylbenzyl)-2-naphthol did not vary from this temperature.

Preparation of Benzal-di-8-naphthol from **β-Naphthol** and I-(a-Dimethylaminobenzyl)-2-naphthol.—Five and one-half grams of 1-(a-dimethylaminobenzy1)-2-naphthol and 3 g. of 8-naphthol were dissolved in the minimum amount of benzene. The solution was slowly heated on a hot-plate and as the benzene evaporated dimethylamine was evolved until a sticky transparent yellow mass was obtained. The sticky substance was dissolved in hot alcohol and on cooling a white crystalline compound separated. It was triturated with warm benzene and filtered. This treatment removed the unreacted 1-(a-dimethylaminobenzy1)-2-naphthol. The compound was then recrystallized twice from alcohol and gave a melting point of 197–198°. A mixed

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[10] Laun, *Ber.*, 17, 678 (1884).

melting point with benzaldi-β-naphthol prepared according to the method of Hewitt and Turners did not vary.

The dimethyl, diethyl and piperidyl derivatives are only slightly basic. They are quite stable and are not affected by light or oxidation. Further work on these compounds including attempts at their resolution is contemplated.

Summary

A study has been made of the condensation of secondary amines with benzaldehyde and β-naphthol and intermediate products in the condensation have been isolated.

It has been shown that the use of amines as catalysts in condensations of a carbonyl with an active methylene may yield first an amine or diamine followed by addition to the active methylene with the formation of a substituted amine, which on further treatment yields the free amine and the final condensation product.

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[CONTRIBUTION PROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

POLYMERIZATION REACTIONS UNDER HIGH PRESSURE. I. SOME EXPERIMENTS WITH ISOPRENE AND BUTYRALDEHYDE

BY J. B. CONANT AND C. O. TONGBERG

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In a preliminary paper[1] on the irreversible transformations of organic compounds under high pressure, some experiments were reported on the polymerization of isoprene and other unsaturated compounds at room temperature by the application of pressures of the order of magnitude of 9000 atmospheres. This work has been continued with the aim of discovering the factors which control the rate of polymerization under high pressures and the nature of the products formed. A great majority of the experiments were performed with isoprene since this substance polymerizes more rapidly than any other substance of this general type which is readily available; furthermore, the early observations showed that very erratic results were obtained with different samples of isoprene and we desired, if possible, to discover the catalytic substances which seemed to be responsible for the peculiar behavior. A few experiments also were performed with some other compounds and they will be discussed at the end of this communication. The pressure apparatus employed was kindly lent us by Professor Bridgman. We wish to express our appreciation of his kind cooperation, and the courtesy extended to us by the Director of the Jefferson Physical Laboratory of Harvard University in which the physical part of the experiments was actually performed. Manipulation of the

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[1] P. W. Bridgman and J. B. Conant, *Proc. Nat. Acad. Sci.*, 15, 680 (1929).

presses was performed by Mr. Zisman and without this valuable assistance the work would not have been possible.

The isoprene used in all of the experiments was prepared by the thermal decomposition of limonene by means of a hot wire, essentially according to the method described by Harries.[2] It was purified by distilling through an efficient column and had a boiling point of 36–38°. The material to be compressed was placed in small glass tubes and pressure transmitted by means of mercury in the apparatus referred to in the previous paper.[1] In most of the experiments the temperature of the press varied between 23 and 25°. The pressure was read by means of the usual device used by Professor Bridgman. The pressures recorded in this paper are usually given in even thousands and are significant within ±100–200 atmospheres. Unfortunately it was not always possible to hold the pressure at exactly the desired point; the actual variations of a few hundred atmospheres probably did not introduce serious errors in the work.

The extent of the polymerization in the case of isoprene was determined by removing the sample from the glass container (if necessary by breaking the container), rapidly weighing, and allowing the material to stand in air until constant weight was obtained. The amount of non-volatile material under these conditions was taken as a measure of the polymerization. This is, of course, only an approximate method but it sufficed for the purposes at hand. The greatest amount of polymerization which we ever observed was 92%. We obtained many figures running between 88 and 90. The fact that 100% was never recorded probably indicates a certain constant error in our method of procedure, although it may correspond to the difficulty of polymerizing the last traces of the isoprene.

It was clear at the outset of our work that the previous history of the isoprene was of great importance in determining the rate of polymerization; for example, some freshly prepared and distilled material was only 30% polymerized in twenty hours at 12,000 atmospheres, whereas some material similarly prepared and distilled which had then been allowed to stand for nine days at 2° in a bottle from which most of the air had been displaced by a stream of nitrogen, was 88% polymerized in the same time and at the same pressure. Oxygen catalysis was, of course, suspected, and the importance of this factor was shown by the fact that it was possible to increase the rate of polymerization by shaking the isoprene with oxygen and then allowing it to stand for some hours. The addition of peroxides and particularly of pinene which had been shaken with oxygen, was very effective in accelerating the rate of polymerization. Hydroquinone, a well-known negative catalyst for reactions subject to oxygen

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[2] C. D. Harries, "Untersuchungen uber die natürlichen und künstlichen Kautschukarten," J. Springer, p. 142.

catalysis, had a marked effect on decreasing the rate; in fact, at 9000 atmospheres pressure it was possible to reduce the rate from 40% in twenty hours to less than 3% in the same time by the addition of about 0.1% hydroquinone. In this experiment a sample of isoprene was used which had been allowed to stand for some time in the presence of oxygen.

Although peroxide catalysis was found to play a very important part in the acceleration of the polymerization, it was not essential to the process. This was demonstrated by the fact that a sample of isoprene carefully distilled in an atmosphere of oxygen-free nitrogen and introduced into the apparatus without the admission of oxygen, nevertheless polymerized under a pressure of 12,000 atmospheres to the extent of 37% in forty-eight hours. It is interesting that at 12,000 atmospheres the presence of 0.1% hydroquinone only changed the rate by about 50%.

Our attempts to measure the effect of pressure and temperature on the rate of polymerization were severely handicapped by the difficulty of preparing uniform samples of isoprene. The use of freshly distilled material did not solve the difficulty as evidently varying amounts of peroxides were formed in an irregular fashion. This is illustrated in Table I. Our most consistent results were obtained with samples of isoprene which had been allowed to stand at 2° in nitrogen or air at least seven days and which then only slowly altered their intrinsic tendency to polymerize. For example, a sample from a given lot which had stood for one day after distilling was 34% polymerized in twenty hours; at the end of the third day another sample from the same lot was 64% polymerized in the same time; on the seventh day the rate had increased to 86% in twenty hours. Further standing up to eleven days seemed to be without effect. A sample from the same lot was freshly distilled on the ninth day and the rate of polymerization dropped from 88% in twenty hours to *25%* in twenty hours. Another lot of material which was allowed to stand under practically the same conditions came to a fairly constant rate which was, however, different from the rate of the first lot; the new maximum rate was about 61% in twenty hours. Still a third lot gave final values nearer the first.

The most significant data which we have so far been able to obtain are given in Table II; the results were obtained with two different lots of isoprene which had stood for at least eight days. An inspection of Table II shows that duplicate experiments usually give very concordant results. This fact at first misled us into believing that it would be possible to determine the rate over the entire range with an accuracy of a few per cent. The results which we later obtained showed that the uncertainties due to catalytic effects, and also caused to a slight extent by the variations in pressure and temperature, made our probable error much greater than we had at first estimated. Some continuous method of following the reaction with one sample for an extended period will have to be developed in order to obtain really satisfactory results.

TABLE I

POLYMERIZATION OF FRESHLY DISTILLED ISOPRENE

Each experiment recorded below was performed with a separate sample of material distilled within one hour of being subjected to pressure

Pressure, 12,000 atmospheres
Temp., 23–25°

Time of application of pressure, hours	Polymerized, %	First order reaction constant, $k \times 10^2$
7	19	3.0
15.25	15	1.1
15.25	12	0.8
29	46	2.1
29	40	1.7
45	25	0.6
68	66	1.6
	Av.	1.6

$k = \frac{2.3}{t} \log \frac{1}{1 - Z}$ where t is in hours and Z is the fraction polymerized.

TABLE II

POLYMERIZATION OF ISOPRENE WHICH HAD STOOD IN NITROGEN CONTAINING A FEW PER CENT. OF OXYGEN AT LEAST NINE DAYS AFTER DISTILLATION

Pressure, 12,000 atmospheres
Temp., 23–25°

Time, hours	Polymerized, %	Reaction constant, $k \times 10^2$
	Lot 1	
5	27	6.3
5	33	8.0
5	35	8.6
16	83	11.2
20	87	10.2
	Av.	8.9
	Lot 2	
5	11	2.3
20	61	4.7
23	66	4.7
23	65	4.6
	Av.	4.1

In order to have some way of comparing the extent of the reaction at different times we have calculated a reaction velocity constant according to the usual first-order equation. The reaction is presumably one of high order but some autocatalytic effect makes the first-order constants actually increase somewhat with time instead of decreasing as would be expected. The result is that they may be used to characterize approximately the rate of the process, and we have used them for this purpose throughout this paper. Some experiments in which indifferent diluents were employed showed that the reaction was actually of an order higher than the first. For example, a sample of isoprene with which it normally took only ten hours for 65% polymerization, required twenty hours for the same extent of reaction when diluted with an equal volume of petroleum ether. The same material when diluted with 5.5 times its volume of petroleum ether or toluene was polymerized to the extent of 5 to 13% in fifteen hours; undiluted, only about one hour would have been required for the same degree of polymerization.

The catalyst which gave the most consistent results was a sample of pinene which had been shaken for four or five hours with oxygen and which was then used from time to time without further treatment. Definite amounts of this pinene were added to freshly distilled isoprene. The results are summarized in Table III, the first order reaction constants being given as a rough measure of the rate of the polymerization. It is evident that the consistency of the results leaves much to be desired but in spite of their variation the effect of the catalyst is evident. The rates obtained with the smallest amount (0.001 per cc. of pinene, a concentration obtained by a dilution procedure) were probably not effective since the average rate of freshly distilled isoprene (Table I) was about the same. The larger amounts of catalyst had a very real effect, although this effect is not directly proportional to the amount; thus an increase of 20-fold in the amount of catalyst only doubled the rate. A few experiments with this same catalyst at pressures of 9000 and 6000 atmospheres indicated the same sort of effect although the results were very erratic at times.

TABLE III

CATALYTIC EFFECT OF OXIDIZED PINENE ON POLYMERIZATION OF FRESHLY DISTILLED ISOPRENE

Pressure, 12,000 **atmospheres. Temp.,** 23–25°

Amount of catalyst, cc. per cc.	Time, hrs.	Percentage polymerized	Reaction constant, k × 10^2
0.1	4.5	83	39.3
.1	4.5	63	22.1
			Av. 30.7
.04	4.5	28	7.3
.04	4.5	41	11.7
.04	4.5	63	22.1
			Av. 13.7
.01	4.5	38	10.6
.01	4.5	12	2.8
.01	16.0	54	4.8
			Av. 6.1
.002	15.75	55	5.1
.002	15.75	55	5.1
			Av. 5.1
.001	4.5	7	1.6
.001	4.5	12	2.8
.001	16.0	24	1.8
			Av. 2.1

We carried out many experiments in an attempt to obtain sufficient information to enable us to give with some accuracy the pressure coefficient of the rate of polymerization; again we have employed the first order constants in comparing the rates. The results are summarized in Table IV. As in all the other work, we were confronted with the difficulty of obtaining reproducible measurements. However, the average value of $k_{12,000}/k_{9000} = 3.5$ is probably of considerable significance. If we assume this value and calculate the ratio of rates for 6000 atm. and 2000 atm. compared to 12,000 from the relationship $A \log k/A P$ = constant, the results are considerably lower than were actually found. Thus, for $k_{12,000}/k_{6000}$ we found 17 and 30 (Table IV, note) while the calculated value is 12. For 2000 atmospheres $k \times 10^2$ for uncatalyzed isoprene is 0.02 (about 2% in five days); this gives a value for $k_{12,000}/k_{2000}$ of about 100 against the calculated 67. As a rough first approximation the effect of pressure seems to be represented from 6000 to 12,000 by the expression $\log k_1 - \log k_2 = 1.8 \times 10^{-4} (P_1 - P_2)$. A very large increase of the pressure coefficient at lower pressures is indicated, however, by the few facts just given and by an extrapolation to atmospheric pressure. Using the equation just given the value of $k_{12,000}/k_1$ is 145 and taking $k \times 10^2$ at 12,000 as 10 (for isoprene after standing), $k \times 10^2$ at 1 atm. = 0.069. This value, which corresponds to 10% polymerization in ten days at 1 atmosphere and 23°, is certainly too large by at least a factor of 100 and probably by 1000 or more. The spontaneous polymerization of isoprene at room temperature and pressure appears to be so slow as to be capable of detection only after a period of years.[3]

TABLE IV

ESTIMATION OF THE PRESSURE COEFFICIENT OF THE RATE OF POLYMERIZATION OF ISOPRENE (TEMP., 23–25°)

Isoprene and catalyst (if any)	Average value of reaction constant 12,000 atm., $k \times 10^2$	9000 atm., $k \times 10^2$	$\frac{k_{12,000}}{k_{9000}}$
Freshly distilled	1.7	Less than 0.2	...
Lot 3, 9 days old	9.0	2.9	3.1
Lot 1, 14 days old	8.9	2.7	3.3
0.1 cc. of pinene	30	7.0	4.3
0.04 cc. of pinene	10	3.5	2.9
0.01 cc. of pinene	6	2.8	2.1
0.01 cc. of pinene	2	0.4	5.0
			Av. 3.5

NOTE.—At 6000 atmospheres a value of $k \times 10^2$ for freshly distilled isoprene was found to be about 0.1 (3% in twenty-six hours), giving a ratio of $k_{12,000}/k_{6000} = 17$. With 0.1 cc. of pinene a value of $k \times 10^2 = 1.0$ at 6000 atm. was obtained (20% in twenty-six hours), giving a ratio of $k_{12,000}/k_{6000} = 30$.

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[3] Since this was written we have unexpectedly been in a position to obtain some additional information in regard to the pressure coefficient. Through the kind cooperation of Professor Bridgeman we have determined the rate of polymerization of isoprene at a pressure of approximately 18,000 ± 500 atm. at 23°; the following amounts of polymer were obtained: 10% in twenty minutes; 76% in three hours; $k \times 10^2 = 52$-65. The same material gave the following values at other pressures: 6000 atm., $k \times 10^2 = 1.9$; 12,000 atm., $k \times 10^2 = 8.4$.

Since the publication of the preliminary paper we have discovered the claims of Herman Plauson to the polymerization of butadiene hydrocarbons at normal temperatures in a few days by applying pressures of the order of 500 to **600** atmospheres. An extrapolation of the results given above to those pressures is not at all consistent with Plauson's results.[4] We have not attempted to repeat all of the six examples given in the Plauson patent but have tried the effect of **600** atmospheres' pressure at room temperature on a mixture of isoprene and dimethylbutadiene emulsified in gelatin solutions as specified and have been able to obtain only the merest trace of possible polymer after six days. Samples of dimethylbutadiene behaved similarly. We are thus unable to confirm the statement that the butadiene hydrocarbons may be polymerized at room temperature by the application of **600** atmospheres' pressure for five to six days.

The temperature coefficient of the rate of polymerization may be estimated from the data given in Table V. If these results are plotted in the usual way (log k against the reciprocal of the absolute temperature) the three points at **12,000** atmospheres fall on a straight line within the probable error. The value of the heat of activation (calculated from the usual equation) is of the order of magnitude of that of simple chemical reactions in solution at room temperatures. The difference in the values at the different pressures cannot be considered as definitely significant in view of the errors in our work. Such an effect may exist but many more experiments at the lower pressures will be necessary to prove it.

TABLE V

TEMPERATURE COEFFICIENT OF THE RATE OF POLYMERIZATION OF ISOPRENE UNDER PRESSURE

Isoprene employed	Average value of reaction velocity constant ($k \times 10^2$)			E calcd. from max. temp. range, calories
	(A) 12,000 atmospheres			
Lot 1 (stood for 13 days)	0.8 (0°)	9.0 (23°)	42 (41°)	16,300
	(B) 9000 atmospheres			
Freshly distilled +0.01 cc. of pinene	...	About 3 (23")	37 (43")	23,000
	(C) 2000 atmospheres			
Isoprene which had stood for 6 days	0.01 (23°)	1.5" (62°)	6.3 (80°)	24,000

[a] Freshly distilled isoprene +0.1 cc. of pinene; value perhaps considerably too high compared to those at 23 and 80°.

A comparison of the temperature and pressure coefficients shows that at the higher pressures and room temperature a change of 15° is about equivalent to **3000** atmospheres' pressure as regards the effect on the reaction rate. Over a wider range we estimate that raising the pressure from

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[4] U. S. patent 1,415,468 (May 9, 1922).

2000 atmospheres to 12,000 atmospheres increases the rate about 100-fold; this increase could also be obtained by raising the temperature from about 20 to 60°. If the temperature and pressure coefficients of the polymerization of isoprene are typical, it is clear that the mere acceleration of the reaction is more readily accomplished by raising the temperature than by increasing the pressure. However, there must be many cases (and the polymerization of isoprene is probably one) where the nature of the products differs according to whether they are formed at high pressures or elevated temperatures. This will evidently be the case when side reactions are possible which have a large temperature coefficient but negligible pressure coefficient. A future field of profitable inquiry into the *acceleration of* reactions by high pressures would seem to be with those complex reactions (such as polymerization) where certain side reactions might be avoided by operating at low temperatures and high pressures.

It has already been emphasized that the polymerization of isoprene under pressure is markedly subject to positive catalysis by oxygen and peroxides and to negative catalysis by hydroquinone. The effect of hydroquinone is more marked at 9000 atmospheres than at 12,000, though the effect of positive catalysts appears to be about the same at the two pressures. The most effective catalyst of all we found to be the isoprene ozonide. For example, if ozonized oxygen (about 5% ozone) was passed into isoprene for twenty minutes and the material then subjected to pressure, the substance was practically completely polymerized (88%) at 12,000 atmospheres in only five hours ($k \times 10^2 = 42$). Although ozone was very effective at this pressure we were disappointed in its action at lower pressures; for example, at 6000 atmospheres it was not so effective as 0.04 cc. of pinene, since in twenty-six hours' time slightly ozonized isoprene was only 5% polymerized. The action of oxygen itself on isoprene is rather peculiar. Freshly distilled material, if shaken with oxygen for a few hours and at once subjected to a pressure of 12,000 atmospheres, polymerizes at about the same rate as though the oxygen treatment had not been given (10–15% in five hours; $k \times 10^2$ about 1). On the other hand, if, after the oxygen treatment, the material is allowed to stand for one to two days, the rate of reaction is greatly accelerated (74–80% in fifteen hours; $k \times 10^2$ about 10). Samples of isoprene which had never been shaken with oxygen but which had stood either in air or nitrogen containing a little oxygen for many days could not be made to polymerize at a faster rate by shaking with oxygen before introducing into the press. From these facts it seems clear that the catalytic action of oxygen is primarily due to a peroxide which is slowly formed from the oxygen dissolved in the isoprene. If an organic peroxide is added directly as in the case of oxidized pinene, or if benzoyl peroxide is used, then there is no indication of an induction period being required. One may imagine that the action of the peroxide is to cause the formation of a series of chain reactions according to the theory which has received such wide acceptance in recent years.

Nature of the Product

In all cases the product obtained at room temperatures was a transparent, colorless, rubbery solid. Its elastic properties, strength and particularly its solubility seemed to be a function primarily of the extent to which the polymerization had been allowed to proceed. Thus the material obtained in runs at 12,000 atm. where the reaction was 80% or more complete was slightly elastic and, though it showed no tendency to crumble, would not stand stretching more than twice its length without breaking. It was extremely insoluble; in fact, we have not found any solvent in which it would dissolve to any appreciable extent. A sample of it was continuously extracted with dry ether in an atmosphere of nitrogen according to the method given by Pummerer;[5] after twelve hours only 1% had been extracted. On the other hand, material from an experiment in which the polymerization was only 30% complete behaved quite differently. After the evaporation of the unpolymerized isoprene the material was very elastic and tough. It could be elongated three to four times without breaking. It was more than 50% extracted by ether in twenty hours and in forty hours was at least 90% soluble. The slight residue was soluble in a benzene–piperidine mixture but not in pure benzene. The density of the polymerized material was about 0.9 as compared with 0.68 for isoprene; thus the volume change in the process is very considerable.

An experiment was performed in order to determine whether the volatile material in an experiment in which the polymerization was incomplete, was wholly isoprene. The excess isoprene (about 50%) was removed by a stream of nitrogen which was then passed through a tube immersed in a carbon dioxide snow-ether mixture. The condensate was examined and found to be practically pure isoprene with only a trace of high-boiling material which had a terpene-like odor. This result, together with all the facts mentioned above, would seem to indicate that the polymerization of the intermediate products must proceed faster than the first step in the process which involves isoprene itself. The extreme insolubility of the completely polymerized material suggests that under these high pressures the reaction proceeds very far even at room temperature. We attempted to see if natural rubber itself would be rendered more insoluble by being subjected to pressure. We employed both crude sheet rubber and the material obtained by extracting this material with ether. In the case of the ether extract there seemed to be some change after subjecting to 12,000 atmospheres for many hours; the resulting material was somewhat less soluble,

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[5] Pummerer, *Ber.*, 61, 1583 (1928).

but the results cannot be regarded as conclusive. More work along this line is in progress. A solution of guttapercha in toluene subjected to 12,000 atmospheres for some hours was apparently unchanged.

Experiments with Other Materials

The rate of polymerization of vinyl acetate is considerably less than that of isoprene; thus in twenty hours at 12,000 atm. the material was only a few per cent. polymerized and even after forty-eight hours only about 50% was converted to the polymer. The effect of oxygen on the rate of polymerization is much less evident than in the case of isoprene; indeed, it is not certain that this polymerization is subject to a positive catalytic effect of this sort. The oxidized pinene catalyst which we found so effective with isoprene had the reverse effect on vinyl acetate, decreasing the rate very markedly. Another strange effect is that the addition of a small quantity of hydroquinone instead of decreasing the rate increased it nearly 10-fold. Because of the long time required in order to obtain appreciable polymerization, the behavior of vinyl acetate was not studied in as much detail as isoprene since the time at our disposal was relatively short.

The peculiar behavior of n-butyraldehyde and isobutyraldehyde was referred to in the preliminary paper.[1] We have now studied the polymerization of n-butyraldehyde in a little more detail. The rate of polymerization is markedly increased by passing ozone through the material for about twenty minutes. Material thus treated was polymerized in twenty-five hours at 12,000 atmospheres to a hard solid amorphous mass without strength or elasticity. This material was evidently of high molecular weight as it was very difficultly soluble in alcohol, ether or other organic solvents. A softer material having the consistency of cheese was obtained by the action of 12,000 atmospheres for twenty-five hours on redistilled aldehyde. In this case the polymerization did not seem to have proceeded so far, since the material was soluble in alcohol. When the alcohol solution was poured into water the material was reprecipitated as an amorphous solid. Both the soft and the hard solids changed rather rapidly on standing at 25°, the eventual product being n-butyraldehyde. The change is definitely catalyzed by the presence of acids and somewhat retarded by the presence of pyridine. However, it was found impossible to keep the material at room temperature for more than about a day even when pyridine was added to it. This rapid reconversion hindered us greatly in studying the material. Attempts to obtain derivatives of the more soluble form by reactions with such reagents as *p*-nitrophenylhydrazine yielded only derivatives of n-butyraldehyde. It seems probable that the products obtained from n-butyraldehyde are polymers similar to the well-known polymers of formaldehyde (trioxymethylene). In the case of formaldehyde the energy relations are such that these polymers of high molecular weight are stable substances at room temperature and pressure, whereas with the higher homologs the complex polymer is perhaps only stable at high pressures. The effect of pressure on the aliphatic aldehydes is in many ways the most interesting result of our work, since it is the one case which have discovered where a reaction can be brought about only by the application of high pressures. We seem to be concerned here not only with increasing the rate of a process but with an actual change of the equilibrium conditions.

Summary

1. The rate of polymerization of isoprene under high pressures has been studied. The reaction is subject to positive catalysis by peroxides and negative catalysis by hydroquinone. Although the reaction is of a high order, the rate is approximately in accord with a first order reaction presumably because of an autocatalytic effect. The temperature and pressure coefficients of the rate have been estimated. The solubility and elasticity of the product depend on the extent to which the isoprene has been polymerized; when the polymerization is practically complete at room temperature at 12,000 atm. the product is very insoluble

2. The action of high pressures on n-butyraldehyde produces a solid only slightly soluble in organic solvents. It reverts to n-butyraldehyde rapidly. It is suggested that this polymer is similar to the well-known polymers of formaldehyde but that the energy relationships are such that the polymer is stable only at high pressures.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, No. 622]

A QUANTITATIVE STUDY OF THE INFLUENCE OF ACETATE AND OF PHOSPHATE ON THE ACTIVITY OF MALT AMYLASE

BY H. C. SHERMAN, M. L. CALDWELL AND IT. H. BOYNTON

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In previous work upon the enzymic activity of malt amylase by different investigators, acetate and phosphate have been used somewhat interchangeably as electrolytes helpful to the activity and conservation of the enzyme. The use of phosphate mixtures, which are not effective buffers at the hydrogen-ion activities employed in work with malt amylase (PH of about 4.5), has probably come about largely through the thought that the phosphate ion is a constant accompaniment of this enzyme when acting in its natural environment and that it may have some specific activating effect. Recent work[1] has shown that the optimal hydrogen-ion activity

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[1] (a) Hahn and Michalik, *Z. Biol.*, 73, 10 (1921); (b) Hahn and Meyer, *ibid.*, 76, 227 (1922); (c) Myrback, *Z. physiol. Chem.*, *149*, 1 (1926); (d) Luers and Nichimura, *Wochschr. für Brauerei, 43, (No. 38)* 415 (1926); (e) Sherman, Caldwell and

for the action of a given enzyme may differ with different environmental conditions, including the kinds and concentrations of electrolytes present, and that, therefore, the apparent influence of an electrolyte may be due to favorable or unfavorable changes in the environment of the enzyme rather than to any specific influence upon the enzyme itself, or that a combination of both these effects may be influencing the results obtained. The experiments here described were, therefore, undertaken with the aim of separating as far as possible the effects of these factors and establishing more definitely the relations of acetate and phosphate to the enzymic activity of malt amylase and to the hydrogen-ion activities which induce its optimal enzymic action.

Experimental

All reagents were carefully purified. A preparation of malt amylase obtained according to a modification of the method of Sherman and Schlesinger[2] was used throughout the work. The method previously described[3] for the determination of the saccharogenic or sugar-forming activity of the enzyme was followed with slight modifications. The enzyme acted in the presence of 2% starch containing known total concentrations of acetate or phosphate. The hydrogen-ion activities of all solutions were measured electrometrically. The general plan of the work involved three steps: first, determinations were made to establish the optimal hydrogen-ion activities for the enzyme when acting in the presence of each of several different concentrations of acetate or of phosphate; second, direct comparisons were made of the activity of the enzyme in the presence of the different concentrations of each salt, when the solutions were in each case adjusted to the optimal hydrogen-ion activity as previously determined; and third, the activity of the enzyme was compared in the absence of any added salt and in the presence of the selected concentration of phosphate or of acetate, each solution being adjusted to the most favorable hydrogen-ion activity.

Results

Relation of Hydrogen-Ion Activity and Concentration of Acetate to the Activity of Malt Amylase.—Direct comparisons were made of the enzymic activity at eight different hydrogen-ion activities between P_H 4.0 and 6.0 in the presence of each of the following total concentrations of acetate: 0.01 M, 0.03 *M*, 0.06 M and 0.1 M. The total acetate concentration was kept con?tant in each case, but the proportions of equimolar acetic acid and sodium acetate used depended on previous electrometric titrations and were changed in order to obtain the desired hydrogen-ion activities. These were verified electrometrically in all cases. The most favorable hydrogen-ion activities were also established in a similar manner for total acetate concentrations of 0.00005 and 0.0001 M.

The averages of several determinations at each concentration of acetate show that the hydrogen-ion activity for the optimal enzymic activity

Dale, THIS JOURNAL, **49**, 2596 (1927); (f) Sherman, Caldwell and Adams, *ibid.*, **49**, 2000 (1927); 50,2529,2535,2538 (1928).

[2] Sherman and Schlesinger, *ibid.*, **35**, 1617 (1913).

[3] Sherman and Walker, ibid, **43**, **2461** (1921).

changes with the concentration of acetate, from PH 4.5 to 4.8 at 0.00005 *M* to PH 5.0 to 5.4 at 0.1 M.

The results of the direct comparisons of the enzymic activity in the presence of the different concentrations of acetate at these optimal hydrogen-ion activities showed that the activity of the enzyme was slightly increased by the lower concentrations of acetate, while the activities at 0.01 to 0.10 *M* showed no significant further increase.

Relation of Hydrogen-Ion Activity and Concentration of Phosphate to the Activity of Malt Amylase.—Similar experiments were made with phosphate mixtures. Again, in each direct comparison, the total phosphate concentration was kept constant, the proportions of phosphoric acid and of acid and alkaline sodium phosphates being changed in order to obtain the desired hydrogen-ion activities. These were verified electrometrically for each solution.

The results are similar to those obtained in the presence of acetate, that is, the optimal hydrogen-ion activity for the enzymic activity changes with the concentration of phosphate from PH 4.5 for 0.00005 M to PH 4.9 for 0.10 M phosphate.

The average results of several direct comparisons of the enzymic activity in the presence of the different concentrations of phosphate at these optimal hydrogen-ion activities show a slight increase in the activity of the enzyme with increasing concentrations of phosphate, but as the phosphate in concentrations higher than 0.01 M seemed to interfere with the accuracy of the determinations of reducing sugar formed, it was not feasible to establish the precise optimum.

Comparison of the Activity of Malt Amylase in the Presence of Acetate and Phosphate.—In order to obtain a quantitative comparison of the activity of the enzyme in the presence of the two salts studied, parallel determinations were carried out, using starch dispersions containing the same concentration, 0.01 *M*, of acetate and of phosphate but adjusted to the optimal hydrogen-ion activity for each case.

The enzyme showed the same activity in the presence of 0.01 *M* acetate or 0.01 M phosphate provided the systems had been adjusted to the optimal hydrogen-ion activity in each case. Inasmuch as acetate and phosphate in appropriate concentration are equally favorable to the action of malt amylase and the acetate is a much more efficient buffer at the hydrogen-ion activities to be used with this enzyme, the acetate is plainly preferable to the phosphate here.

Summary

The optimal hydrogen-ion activities for malt amylase in the presence of different concentrations of acetate and of phosphate have been quantitatively established and found to depend on the concentration of the salt.

Even in very low concentrations, both acetate and phosphate increase the activity of malt amylase slightly.

Acetate, well known to be much the more efficient buffer in the range of hydrogen-ion activities suitable for work with this enzyme, is here found to be as effective in activating the enzyme as is phosphate, and to be experimentally applicable over a wider range of concentration.

Acetate is, therefore, preferable to phosphate as a buffer salt for use with malt amylase.

In an acetate concentration of 0.01 M the optimal activity was found at P_H 4.5 to 4.8, and in a concentration of 0.1 M, at P_H 5.0 to 5.4.

NEW YORK, N. Y.

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

THE CONSTITUTION OF CATECHIN. X

BY M. NIERENSTEIN

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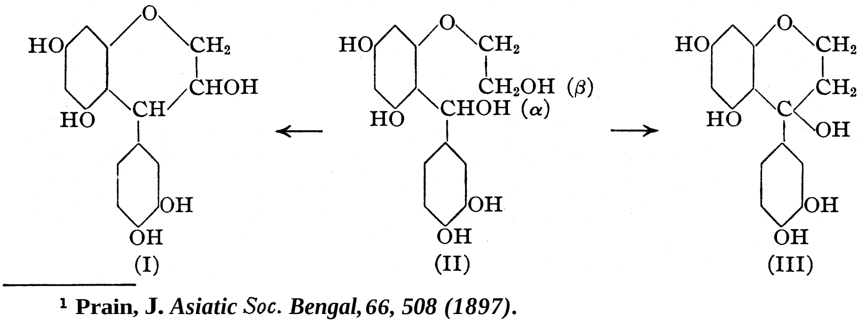
Only the heart-wood of the cutch-producing acacias,[1] Acacia Catechu, Willd., *A.* Catechuoides, Benth. and A. *Sundra,* D. C. is used in the manufacture of cutch, since it is generally believed that the other parts of the plant contain no catechin.[2] An examination of the sap-wood, bark and young twigs of these three acacias, carried out in this Laboratory, supports this generally accepted view. Furthermore, it was found that the catechin content of the heart-wood increases as the medulla is approached, which would seem to indicate that catechin is a final product of metabolism in these acacias,[3] and must therefore be derived from some other product formed in the living plant. This hypothesis is confirmed by the presence of l-leucomaclurin-glycol ether (II) in the young twigs of Acacia Catechu, Willd. The production of acacatechin (I) and iso-acacatechin (III) from *l*-leucomaclurin-glycol ether (II) would then follow as a matter of course.



(I) (II) (III)

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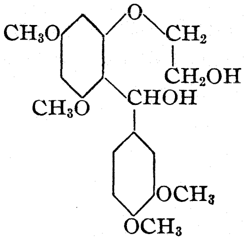
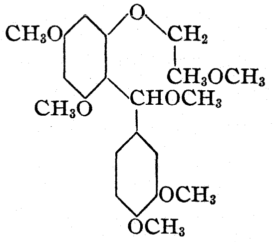
[1] Prain, J. *Asiatic Soc. Bengal,* 66, 508 (1897).

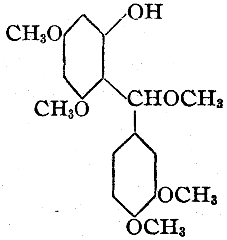
[2] Wiesner, "Die Rohstoffe des Pflanzenreiches," 3d ed., Leipzig und Berlin, 1914, Vol. I, p. 605.

[3] These considerations obviously do not apply to gambier-catechin present in the leaves of *Umcaria Gambier* and allied species.

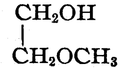
Substance II yields on methylation with diazomethane a tetramethyl ether to which Formula IV can be assigned with some degree of certainty, since the two aliphatic hydroxyl groups marked α and β, respectively, would not react with diazomethane.[4] On methylation of Substances II and IV with methyl iodide and silver oxide, the hexamethyl ether (V) is produced, which yields on hydrolysis pentamethyl-leucomaclurin (VI) and monomethyl-glycol (VII).


(IV)

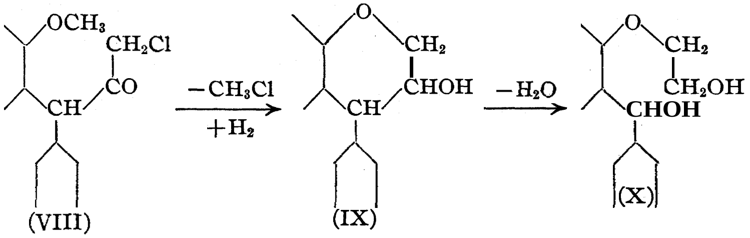

(V)


(VI)

+


$$\begin{array}{l}CH_2OH\\ |\\ CH_2OCH_3\end{array}$$
(VII)

On acetylation by heating with acetic anhydride l-leucomaclurin-glycol ether (II) yields penta-acetyl-*l*-acacatechin (I), this being further evidence for the constitution of acacatechin, which is produced from *l*-acacatechin on racemization. The acacatechin nucleus, (IX), has thus been built up along two different lines: (1) by ring closure of (VIII) followed by reduction of the carbonyl group as recorded in 1921 and 1926;[5] (2) by ring closure of (X) as described in the present communication. These results obviously substantiate no other formula for catechin but that suggested by the writer in 1920.[6]



Reference must be made to the fact that although during the conversion of 1-leucomaclurin-glycol ether into penta-acetyl-*l*-acacatechin a new asymmetric carbon atom is produced, no other product but penta-acetyl-*l*-acacatechin could be detected. This can only be accounted for by the

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[4] With reference to hydroxyl group α see: Nierenstein and co-workers, J. *Chem. Soc.*, 107, 1491 (1915); 109, 596 (1916); 117, 975, 1598 (1920); THIS JOURNAL, 46, 2553, 2804 (1924). With reference to hydroxyl group β see: Pechmann, *Ber.*, 27, 1888 (1894); 28, 857 (1895); Werner, *J. Chem. Soc.*, 115, 1098 (1919); Biltz and Paetzold, *Ann.*, 433, 86 (1923); Nierenstein, *Ber.*, 60, 1820 (1927).

[5] Nierenstein, *J. Chem. Soc.*, 119, 167 (1921); THIS JOURNAL, 48, 1964 (1926).

[6] Nierenstein, *ibid.*, 117, 974 (1920).

assumption suggested to the writer by Professor J. Meisenheimer of Tübingen, and Dr. W. H. Mills, F.R.S., of Cambridge, that the other stereoisomeric form is produced in such a small quantity (less than 1% as evident from several attempts to isolate it) that it escapes detection.

Experimental

The twigs used in this investigation were sent by courtesy of the authorities of the Forest Research Institute in Dehra Dun, India. They arrived in two consignments in 1921 and 1924, respectively. Each consignment was investigated separately and identical products were obtained from both, a total of 850 kilos of finely powdered young twigs being examined.

I-Leucomaclurin-glycol Ether.—The most striking difference between this substance and catechin is that *l*-leucomaclurin-glycol ether is very soluble in cold water, which accounts for the fact that it has so far been overlooked. For the extraction 5 liters of distilled water per kilo of powdered twigs are used and a little chloroform added to prevent infection. The pressed out and filtered extracts are decolorized with lead acetate, a little lead carbonate being added, and the filtered solution freed from lead with the aid of hydrogen sulfide. The filtrate from the lead salt is boiled, filtered when cold, and concentrated in *vacuo* to about 50 cc., when, on standing, faintly yellow-colored crystals are deposited. In this manner from 1 kilo of the powdered twigs a maximum yield of 0.5 g. of crude product is obtained. The total yield of crude material obtained from 850 kilos of powdered twigs is 182 g. For further purification 3 g. of the product is dissolved in 50 cc. of distilled water, to which a few drops of acetic acid are added, boiled with a little charcoal and the filtered solution left slowly to evaporate over concd. sulfuric acid. This process is best repeated twice; yield of pure product, 114 g.

I-Leucomaclurin-glycol ether (II) crystallizes in microscopic needles, which melt at 198" without previous sintering when pure, although some darkening may be observed at about 170–180°. It is easily soluble in water, alcohol, acetone and ether. The aqueous solution turns green with ferric chloride, yellow on warming with alkali and gives a deep red coloration on pine wood when tested with phloroglucinol. In this respect it differs from catechin, which gives a purplish coloration for phloroglucinol. The following rotations are given by *l*-leucomaclurin-glycol ether: $[\alpha]_D^{19}$ —62.57 (in water), $[\alpha]_D^{19}$ —41.59 (in alcohol), $[\alpha]_D^{18}$ —11.48 (in acetone).

Anal. (I) Freshly crystallized, air-dry material dried in a vacuum over phosphorus pentoxide at 100". Subs., 13.14, 11.61 mg.: H_2O, 2.36, 2.07 mg. Calcd. for $C_{15}H_{16}O_7 + 4H_2O$: H_2O, 18.95. Found: 17.96, 17.83. (II) Material dried in desiccator over calcium chloride. Subs., 7.812, 5.924 mg.: CO_2, 14.810, 11.325 mg.; H_2O, 4.165, 3.139 mg. Calcd. for $C_{15}H_{16}O_7 + 2H_2O$: C, 52.33; H, 5.81. Found: C, 51.71, 52.15; H, 5.97, 5.93. (III) Anhydrous material, obtained by drying in a vacuum over phosphorus pentoxide at 100°. Subs., 9.54, 10.78 mg.: CO_2, 20.41, 23.08 mg.; H_2O, 4.47, 5.07 mg. Calcd. for $C_{15}H_{16}O_7$: C, 58.44, H, 5.20. Found: C, 58.35, 58.39; H, 5.24, 5.26.

Tetramethyl Ether (IV).—To a suspension of 1 g. of anhydrous *l*-leucomaclurin-glycol ether in 100 cc. of ether is added an ethereal solution of diazomethane from 8 cc. of nitrosomethylurethan. The residue (1.1 g.) left on evaporation of the ether crystallizes from alcohol in colorless pointed needles which melt at 147". The product is soluble in the usual organic solvents, but quite insoluble in water, the alcoholic solution giving no coloration with ferric chloride. The following rotations are observed: $[\alpha]$: —36.40° (in alcohol), $[\alpha]_D^{16}$ —22.20' (in 50% acetic acid).

Anal. Subs., 11.26 mg.: CO_2, 25.79 mg.; H_2O, 6.81 mg. Subs., 3.21 mg.; AgI, 8.24 mg. Calcd. for $C_{19}H_{24}O_7$: C, 62.64; H, 6.59; OCH_3, 34.07. Found: C, 62.46; H, 6.77; OCH_3, 33.89.

Hexamethyl Ether (V).—The methylation both of substances (II) and (IV) is carried out by suspending the products in an excess of methyl iodide diluted with twice its volume of anhydrous ether and adding the theoretical amount of silver oxide, calculated on the methyl iodide used. Soon after the silver oxide is added, the reaction sets in and is completed by refluxing on a water-bath until the odor of methyl iodide disappears, which requires about one and one-half to two and one-half hours. The filtered solution is evaporated and the solid obtained dissolved in alcohol, filtered from a flocculent by-product and precipitated with water, when a nearly theoretical yield of the crude hexamethyl ether (V) is obtained. It crystallizes from alcohol in small needles and from benzene and ligroin (1:1) in long prismatic needles. It melts sharply at 97°. The product is soluble in all organic solvents, but quite insoluble in water. It is optically active, the following values being obtained: $[\alpha]_D^{19}$ −63.40° (in alcohol), $[\alpha]_D^{19}$ −35.99° (in acetone), $[\alpha]_D^{17}$ −74.55° (in carbon tetrachloride).

Anal. Subs., 10.06 mg.: CO_2, 23.67 mg.; H_2O, 6.53 mg. Subs., 2.76 mg.: AgI, 9.98 mg. Calcd. for $C_{21}H_{28}O_7$: C, 64.29; H, 7.14; OCH_3, 47.45. Found: C, 64.17; H, 7.26; OCH_3, 47.73.

Hydrolysis of the Hexamethyl Ether (V).—To a solution of 5 g. of substance (V) in 50 cc. of methyl alcohol is added 20 cc. of a 25% solution of sodium in methyl alcohol and the mixture refluxed for five hours. The greater part of the alcohol is removed on evaporation and the product obtained is steam distilled, the distillate being freed from alcohol by warming on the water-bath and then extracting with ether. The dried ethereal solution is evaporated to dryness, the residue dissolved in 5 cc. of dry pyridine and treated with 3 g. of triphenylchloromethane according to Helferich, Speidel and Toeldte.[7] In this manner 2.1 g. of crude methyltriphenylmethylglycol is obtained. The product crystallizes from alcohol in big needles which melt at 104°, the melting point not being depressed on admixture with authentic methyltriphenylmethylglycol.[8]

Anal. Subs., 8.68 mg.: CO_2, 26.39 mg.; H_2O, 5.49 mg. Subs., 6.22 mg.; AgI, 4.66 mg. Calcd. for $C_{22}H_{22}O_2$: C, 83.02; H, 6.92; OCH_3, 9.75. Found: C, 82.92; H, 7.08; OCH_3, 9.89.

The solution from which the methyl glycol has been removed on steam distillation is acidified and extracted with ether. The dried ethereal solution is filtered and treated with excess of an ethereal solution of diazomethane. The solid left on evaporation of the ether crystallizes from alcohol in colorless needles which melt at 103°, the melting point not being depressed on admixture with authentic hexamethyl-leucomaclurin prepared according to Kostanecki and Lampe.[9]

Anal. Subs., 7.82 mg.: CO_2, 18.76 mg.; H_2O, 4.88 mg. Subs., 2.71 mg.; AgI, 11.16 mg. Calcd. for $C_{19}H_{24}O_6$: C, 65.52; H, 6.89; OCH_3, 53.45. Found: C, 65.42; H, 6.98; OCH_3, 54.36.

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[7] Helferich, Speidel and Toeldte, *Ber.*, 56, 766 (1923).

[8] Nierenstein, *Ber.*, 60, 1821 (1927).

[9] Kostanecki and Lampe, *Ber.*, 39, 4021 (1906). The melting point given by these authors is 94–96° for the product prepared by the action of veratroyl chloride on trimethylphloroglucinol, reduction of pentamethylmachurin to the leuco product and methylation of the latter. The product obtained by me melted, however, at 103°. For comparison hexamethyl-leucomaclurin was also prepared by methylation of maclurin with dimethyl sulfate as well as methyl iodide in methyl alcoholic solution. These two products also melted at 103° and gave correct analytical data.

Production of Penta-acetyl-*l*-acacatechin from I-Leucomaclurin-glycol Ether.—A solution of 5 g. of *l*-**leucomaclurin-glycol** ether in an excess of acetic anhydride is heated for forty minutes and the cold solution poured into water. The white solid formed on **standing** melts in the crude state at **149–151°** and is practically pure penta-acetyl-l-acacatechii, which **crystallizes** from alcohol in needles melting at 151°. This melting point is not depressed when penta-acetyl-*l*-acacatechin from *l*-leucomaclurin-glycol ether is mixed in varying proportions with the penta-acetyl derivative of 1-acacatechin from the heart-wood of *Acacia Catechu,* Willd. The rotation of penta-acetyl-*l*-acacatechin from I-maclurin-glycol ether in tetrachloro-ethane is $[\alpha]^{21}_{D}$ −12.0°, whereas penta-acetyl-*l*-acacatechin from I-acacatechin rotates in the same solvent $[\alpha]^{20}_{D}$ −11.5°, the same concentration being used in both cases.

Anal. Subs., 5.222, 4.642 mg.: CO_2, 11.376, 10.171; H_2O, 2.397, 2.084 mg. Calcd. for $C_{25}H_{24}O_{11}$: C, 60.00; H, 4.80. Found: C, 59.41, 59.76; H, 5.14, 5.02.

For the greater part of the analytical data the author is indebted to Miss Christina M. Fear. He also wishes to thank the Colston Research Committee of the University of Bristol for a grant which has covered the expenses of the investigation.

Summary

It is shown that the young twigs of *Acacia Catechu,* Willd. contain *l*-leucomaclurin-glycol ether, which on acetylation yields penta-acetyl-l-acacatechin, the acetyl derivative of the catechin present in the heart-wood of this tree.

BRISTOL, ENGLAND

[CONTRIBUTION FROM THE ABBOTT LABORATORIES]

5,s-SUBSTITUTED BARBITURIC ACIDS[1]

BY E. H. VOLWILER AND D. L. TABERN

RECEIVED DECEMBER 26, 1929 PUBLISHED APRIL 7, 1930

Of the many types of chemical compounds which can produce sleep, the derivatives of barbituric acid continue to be by far the most important. During recent years, the availability of new alcohols has made possible the more systematic study of the homologs of the parent member of the series, barbital (diethylbarbituric acid), with the result that several new hypnotics of superior therapeutic merit have become available. More than a hundred barbituric acid derivatives have been synthesized and most of them have been pharmacologically tested; a number of them have found their way into clinical use.

Considerable variation in sleep-producing activity exists among the members of this series, ranging from none at all to over four times that of barbital. If this increase in efficiency over barbital were merely accompanied by a corresponding increase in toxicity, there would be little attained by the study of the newer barbituric acid derivatives. This is not neces-

[1] Presented before the Medicinal Products Division of the American Chemical Society at Minneapolis, Sept. 10, 1929.

sarily the caw, however, for experiments on animals have shown that sleep-producing efficiency and other pharmacological properties may not vary to the same degree as toxicity. This is to be expected, for solubilities, rates of absorption and elimination, etc., would be likely to be different for various members of the series. These observations are also of interest in connection with the intravenous use of certain barbiturates for the production of general anesthesia.

From the study of scores of these new barbituric acid derivatives, it has been possible to arrive at some conclusions regarding the pharmacologic effects of lengthening the saturated hydrocarbon radicals on the carbon atom in the 5-position,[2] the influence of unsaturation in these radicals[3] and the effect of substitution on the nitrogen of the barbituric acid nucleus.[4] Also, the results produced by other modifications have been studied, such as the substitution of cyclic structures, halogens, ether groups, amino radicals, etc.

Up to the present time, the study of the effects of alkyl groups has been limited largely to homologs, and comparatively little attention has been given to the results produced by isomerism of the alkyl groups. This is due to the fact that until recently few isomeric alcohols beyond the butyl series have been available. In the latter series, the normal, iso and secondary butyl radicals have been introduced into barbituric acid and the pharmacologic effects carefully observed; attempts to prepare tertiary butyl substituted barbituric acids have failed.

The present availability of isomeric amyl alcohols has made possible a somewhat more extended comparative study of the effects of isomerism on hypnotic action. In addition to the normal and iso-amyl alcohols, the following alcohols are now commercially available: 1-methylbutyl alcohol, 2-methylbutyl alcohol and 1-ethylpropyl alcohol.

The following amyl substituted barbituric acids have previously been prepared: n-amyl, di-n-amyl and n-amyl ethyl;[5] iso-amylmethyl, iso-amylethyl, iso-amyl-n-propyl, iso-amylisopropyl and di-iso-amyl;[6] iso-amylallyl;[3] ethyl-(1-ethylpropyl) and ethyl-(1-methylbutyl).[7]

In addition to the new isomeric amylbarbituric acid compounds which have now been prepared, two octyl derivatives were added to the list for comparison.

These compounds were tested, in comparison with barbital as a standard and with certain other known barbituric acid derivatives, by subcutaneous

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[2] Tiffeneau, *Bull. soc. chim.*, [4] 33, 183 (1923).

[3] Volwiler, THIS JOURNAL, 47, 2236 (1925).

[4] Dox and Hjort, *J. Pharm. Exptl. Therap.*, 31, 455 (1927).

[5] Dox and Jones, THIS JOURNAL, 50, 2033 (1928).

[6] Carnot and Tiffeneau, *Compt. rend.*, 175, 242 (1922); Shonle and Moment, THIS JOURNAL, 45, 243 (1923).

[7] German Patent 293,163; Friedlander, 13, 800 (1916–1921).

injections of solutions of the sodium salts according to the method previously described.[3,8]

Of this series of compounds, the most efficient are the ethyl-(1-methylbutyl) and the ethyl-(2-methylbutyl) derivatives. In sleep-producing efficiency in rats, the former compound seems to be the most active saturated alkylbarbituric acid that has been prepared. It is of interest that it is appreciably more efficient when tested on rats than the corresponding normal or iso compounds. These results also confirm the previously reported findings among the higher homologs of the barbituric acid series that increasing the size of the second alkyl group causes a decrease in hypnotic efficiency. Some comparative data, obtained by subcutaneous injections into rats, are given in the following table; an asterisk indicates that the data are taken from the literature.

	Hypnotic efficiency (Barbital = 1)		Hypnotic efficiency (Barbital = 1)
Ethyl-n-amyl	2.5	Di-n-amyl	0*
Ethyl-iso-amyl	3	Di-iso-amyl	1*
Ethyl-(2-methylbutyl)	3+	Allyl-*n*-amyl	1.25
Ethyl-(1-methylbutyl)	4.5	Allyl-iso-amyl	2.3+

Experimental Part

The intermediate malonic esters were prepared in the usual manner by the reaction of the alkyl bromide with malonic ester in the presence of sodium ethylate. The yields were from 70 to 85% of the theoretical. The disubstituted barbituric acids were prepared as usual by the reaction of the required disubstituted malonic ester with urea at 80–85°, in the presence of sodium ethylate. Most of the products were purified by recrystal-

TABLE I

PROPERTIES OF BARBITURIC ACID DERIVATIVES

		Properties of derivatives		
			Nitrogen, %	
Derivatives	Recryst. from	M. p., °C.	Calcd.	Found
n-Amylallyl	Water	97–100	11.76	11.78
Ethyl-(2-methylbutyl)	Pptd. from Na salt by CO_2	135–136	12.39	12.31
n-Butyl-(2-methylbutyl)	Dil. alcohol	146–148	11.03	10.91
n-Butyl-n-amyl	Alc., then pptd. from K salt by CO_2	118–120	11.02	10.80
Isopropyl-n-amyl	Water	100–102	11.67	11.57
Isobutyl-n-amyl	Alcohol	105–107	11.03	11.13
Isobutyl-iso-amyl	50% alcohol	146–147	11.03	10.90
Allyl-(2-methylbutyl)	Water	97–99	11.76	11.51
n-Butyl-(1-ethylpropyl)	Water	108–109	11.03	10.81
Ethyl-(1-methylbutyl)	Alcohol	129–130	12.39	12.36
n-Butyl-(1-methylbutyl)	Dil. alcohol	111–112	11.03	10.85
n-Butyl-(1-methylheptyl)	Dil. alc. or water	Indef.	9.45	9.35
Allyl-(1-methylheptyl)	Water or dil. alc	148–150	10.0	10.4

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[8] Nielsen, Higgins and Spruth, *J. Pharmacol. Exptl. Therap.*, 26, 371 (1925).

TABLE I (Concluded)

PROPERTIES OF CORRESPONDING MALONIC ESTERS

Name	B. p., °C.	Mm.	Refr. index	Name	B. p., °C.	Mm.	Refr. index
n-Amyl	134–136	14	1.4240	*n*-Amyl-allyl	190–195	50	1.4372
2-Methylbutyl	150–152	45	1.4235	Ethyl-(2-methylbutyl)	160–165	37	1.4324
n-Butyl	235–240	760	1.4250	n-butyl-(2-methylbutyl)	165–170	22	1.4330
n-Butyl	235–240	760	1.4250	*n*-Butyl-*n*-amyl	185–193	55	1.4312
Isopropyl	211–215	760	1.4180	Isopropyl-n-amyl	186–190	50	1.4320
n-Amyl	134–136	14	1.4240	Isobutyl-n-amyl	184–192	47	1.4327
Iso-amyl	160–165	44	1.4230	Isobutyl-iso-amyl	170–176	35	1.4316
2-Methylbutyl	150–152	45	1.4235	Allyl-(2-methylbutyl)	154–167	26	1.4360
n-Butyl	235–240	760	1.4250	*n*-Butyl-(1-ethylpropyl)	155–170	40–50	1.4353
Ethyl	207–210	760	1.4200	Ethyl-(1-methylbutyl)	133–140	14	1.4329
n-Butyl	235–240	760	1.4250	*n*-Butyl-(1-methylbutyl)	145–150	20	1.4310
n-Butyl	235–240	760	1.4250	*n*-Butyl-(1-methylheptyl)	185–190	16	1.4410
1-Methylheptyl	195	57	1.4310	Allyl-(1-methylheptyl)	165	10	1.4370

TABLE II

SOLUTIONS OF THE SODIUM SALTS INJECTED SUBCUTANEOUSLY INTO WHITE RATS, EXPRESSED IN MILLIGRAMS OF THE BARBITURIC ACID PER KILOGRAM OF BODY WEIGHT

Batbituric acid derivative	Minimum effective dose (not awakened when outer ear passage is tickled with a straw)	Minimum lethal dose	Ratio $\frac{\text{M. E. D.}}{\text{M. L. D.}}$
n-Amylallyl	160	250	0.64
Ethyl-(2-methylbutyl)	60	160	.375
n-Butyl-(2-methylbutyl)	Above 600	Above 600	
n-Butyl-n-amyl	Above 600	Above 600	
Isopropyl-n-amyl	150	290	.52
Isobutyl-n-amyl	410	Above 600	
Isobutyl-iso-amyl	400–450	Above 600	
Allyl-(2-methylbutyl)	80	170	.47
n-Butyl-(2-methylbutyl)	300–500	500	
Ethyl-(1-methylbutyl)	40 to 50	110	.41
Allyl-(1-methylheptyl)	Above 400	Above 400	
Diethyl	225	310	.72

lization from alcohol or water or a mixture of the two; in some cases purification was accomplished by dissolving the compounds in alkali and precipitating with acetic acid or carbon dioxide.

Summary

1. A series of isomeric amyl substituted barbituric acids has been prepared and the hypnotic activities pharmacologically compared.

2. The most effective of this series of compounds, injected subcutaneously in rats, are ethyl-(1-methylbutyl)-barbituric acid and ethyl-(2-methylbutyl)-barbituric acid.

NORTH CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE HYGIENIC LABORATORY, UNITED STATES PUBLIC HEALTH SERVICE]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XXV. THE RING STRUCTURES OF VARIOUS MONOSACCHARIDES[1]

BY C. S. HUDSON

RECEIVED JANUARY 8, 1930 PUBLISHED APRIL 7, 1930

1. Four years ago the writer[2] published a critical examination of the rotations of many substances in the mannose and rhamnose series which had previously been considered as exceptions to the rules of optical superposition and isorotation.[3] It was shown that while many pairs of these substances exhibit comparative rotations that are abnormal, many other pairs show close conformity with the rules. To account for this significant fact, there was proposed the hypothesis *that among the known derivatives of mannose and rhamnose there occur substances of various ring types (which accounts for the observed exceptional comparative rotations) and that substances belonging to the same ring type show normal comparative rotations (which accounts for the normal values).* As a consequence of this view the substances in these series were allocated to three types, the rings of which were designated 1,A, 1,B and 1,C. The question of the assignment of positions A, B and C to particular carbon atoms was left open in so far as the use of arguments based upon rotatory relations is concerned.

2. In an accompanying article[4] it was then sought to determine the positions of A and B by the use of results that had been obtained shortly before from methylation studies by several workers, who had shown that normal methyl xyloside,[5] galactoside[6] and arabinoside[7] must possess a 1,5-ring provided the assumption that rings do not shift during methylation is correct. This assumption had never been questioned and no evidence was known against it, though on the other hand its validity had never been

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[1] Publication authorized by the Surgeon General, U. S. Public Health Service. Presented at the Organic Symposium of the American Chemical Society, Princeton, New Jersey, January 1, 1930. No. XXIV of this series was published in THIS JOURNAL, 52, 1270 (1930).

[2] Hudson, *ibid.*, **48**, 1424 (1926).

[3] Hudson, ibid., 31, 66 (1909); Scientific Papers of the Bureau of Standards, No. 533 (1926). In the latter paper (pages 245–249) the distinction between optical superposition and isorotation is discussed; the paper is obtainable from the Superintendent of Documents, Government Printing Office, Washington, D. C., price, 35 cents.

[4] Hudson, THIS JOURNAL, **48**, 1434 (1926).

[5] Hirst and Purves, *J. Chem. Soc.*, 1352 (1923).

[6] Pryde, *ibid.*, 1808 (1923).

[7] Hirst and Robertson, *ibid.*, 358 (1925).

definitely established in the case of any glycoside.[8] Using these 1,5-ring allocations for the xyloside, galactoside and arabinoside, the writer showed that the rotatory powers of the alpha and beta forms of methyl glucoside of the same 1,5-ring structure can be deduced through the rules of isorotation; the values so calculated were widely different from the rotations of the known normal methylglucosides and it was concluded that the 1,5-ring does not occur in the latter. Since other methylation data, to which reference was there made, limited the ring to the 1,4- and 1,5-positions, it was inferred that the normal methylglucosides possess the 1,4-ring. The same result followed from the similar consideration of the rotations of the fully acetylated derivatives of the glycosides mentioned.

3. This ring assignment for the glucosides conflicted with the results which Charlton, Haworth and Peat[9] had published shortly before; their studies indicated that normal tetramethylglucose possesses the 1,5- rather than the 1,4-ring and that the like structure pertains to the normal methylglucosides on the assumption that methylation does not cause ring-shifting. If the writer's argument for the 1,4-ring structure of these glucosides had been limited to the data that have been summarized in paragraph 2, it is probable that publication would not have been made in view of the conflict with the results of Charlton, Haworth and Peat, because this disagreement could be accounted for by questioning the applicability of the isorotation rules to the case in hand, particularly the assumption that r_4, the rotation of Carbon 4, has the same value in the pentoside and hexoside structures. This assumption, while not derivable from the rule of optical superposition, appeared probable to the writer from the large number of cases where the rules of isorotation, by which the assumption could be supported, had been found to hold fairly closely. It was emphasized in the article that objection might be made to the assumption but *it was shown that it led to the prediction of values for the rotations of unknown substances the correctness of which could be supported by independent evidence.* Thus it was found that the calculated rotations of the unknown methylglucosides fit accurately, along with the rotations of the known forms, in the system of ring structures that had just been developed for the mannose and rhamnose series, as epimers of the methylmannosides of the 1,A and 1,B ring structures, respectively. The rotations of the acetates of these various glycosides showed the same correlation. Because of the support which these independent results gave to the assumption that r_4 has the same rotation in the pentosides and hexosides, the writer decided to publish the calculations, which indicated that the 1,A ring is 1,5, the 1,B ring is 1,4 and that the

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[8] The word glycoside is used in the generic sense to include glucoside-like derivatives of any of the aldoses or ketoses; the term glucoside is limited to the glycosides of the particular sugar glucose.

[9] Charlton, Haworth and Peat, J. *Chem. Soc.*, 89 (1926).

normal methylglucosides have the 1,4-ring, and to leave to the future the discernment of the reason for the disagreement with the results of Charlton, Haworth and Peat concerning the ring position in the glucosides.[10]

4. The existence of this disagreement prompted the writer to seek new experimental evidence which might disclose its cause. It was early recognized that the value of the epimeric difference of rotation sharply distinguishes the viewpoints of the rival classifications of rings and that decision between the two systems might be obtainable from measurements of the rotations of a pair of substances having configurations that could be epimeric but in which only one of the two rings 1,4 and 1,5 could be assumed to exist. Such a pair of substances would be represented, for instance, by cellobiose and 4-glucosido-mannose because Zemplén[11] had proved by evidence which did not involve methylation that cellobiose is 4-glucosido-glucose and Bergmann and Schotte[12] had synthesized the epimeric 4-glucosido-mannose from cellobiose by reactions which did not sever the disaccharide union. In these sugars the 1,4-ring for the reducing hexose molecule is excluded and only the 1,5-ring is probable; their rotations should in consequence give the correct value for the epimeric difference of rotation. Another pair of sugars to which the same argument applies is lactose[13] and 4-galactosido-mannose.[14] One is not restricted to the sugars themselves but can also employ suitable acetylated derivatives, as is evident from the writer's table[4] in which the values of the molecular epimeric difference for the sugars ($2r_2$ = 6700) and for their acetylated derivatives ($2R_2$ = 11,300) were shown. Plans were accordingly made for obtaining the necessary substances in pure form. By a fortunate circumstance, however, the appropriate data became available within a few months after the appearance of the writer's article through a publication by D. H. Brauns[15] of the carefully measured rotations of four pure acetohalogeno

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[10] Drew and Haworth [J. Chem. *Soc.*, 2303 (1926)] later sought to explain the disagreement by questioning the validity of the assumption regarding r_4, without mentioning, however, that the writer had raised the same question and had considered that he had answered it by adducing the independent evidence referred to above. This evidence, which they have passed over, seems of far more significance than the purely speculative discussion of the twisting of ring structures and carbon valences by which they have sought to show that r_4 should have different values in the pentoside and hexoside structures. However, it will be shown presently (paragraph 5) that the cause of the disagreement is a matter that is quite apart from the question of the constancy of the value of r_4, and (paragraph 16) that the assumption of constancy can be supported by further independent evidence. In regard to a second matter that Drew and Haworth presented, concerning some supposed evidence on the ring structures in the galactose and glucose series, see paragraph 22.

[11] Zemplén, Ber., 59, 1254 (1926).

[12] Bergmann and Schotte, *ibid.*, 54, 1564 (1921).

[13] Zemplén, *ibid.*, *60,* 1309 (1927).

[14] Bergmann, *Ann.*, *434,* 79 (1923).

[15] Brauns, THIS JOURNAL, 48, 2776 (1926).

derivatives of 4-glucosido-mannose. The epimeric difference is obtainable from these measurements in conjunction with Brauns' other measurements[16] of the rotations of the analogous derivatives of cellobiose. The comparisons are shown in Table I. The good agreement of the values in the last column is evidence that the isorotation rules apply closely among these pairs; the greatest deviation from the mean represents only two or three degrees in specific rotation. The average value of $2R_2$ (11,800) agrees closely with the writer's original determination[4] from the rotations of acetylated substances of the glucose and mannose series (11,300); on the other hand, the ring assignments of Haworth lead to a far different value for $2R_2$ (29,500), obtained from the molecular rotations of the tetraacetates of normal α-methylglucoside[4] (47,300) and normal a-methylmannoside[4] (17,800).

TABLE I

THE EPIMERIC DIFFERENCE OF MOLECULAR ROTATION FOR ACETYLATED DERIVATIVES OF THE CELLOBIOSE AND 4-GLUCOSIDO-MANNOSE SERIES (D. H. BRAUNS' DATA)

Substance	$[\alpha]^{20}_D$ in $CHCl_3$	$[M]^{20}_D$	Epimeric difference ($2R_2$)
a-Acetofluorocellobiose	30.6	19,520	10,840
α-Acetofluoro-4-glucosido-mannose (mol. wt. 638)	13.6	8680	
a-Acetochlorocellobiose	71.7	46,960	13,420
a-Acetochloro-4-glucosido-mannose(mol. wt. 655)	51.2	33,540	
a-Acetobromocellobiose	95.8	66,970	12,520
a-Acetobromo-4-glucosido-mannose (mol. wt. 699)	77.9	54,450	
a-Aceto-iodocellobiose	125.7	93,770	10,590
a-Aceto-iodo-4-glucosido-mannose (mol. wt. 746)	111.5	83,180	
	Average	$2R_2$	11,800

5. This crucial test convinced the writer at the time when Brauns' article appeared (1926) that Haworth's assignment of the same ring to the normal methylglucoside and mannoside must be invalid. In consequence a choice between the following alternative views appeared necessary: either (1) the chemical studies on the tetramethyl derivatives of glucose and mannose by Haworth and his collaborators contain some faulty identification which invalidates his conclusion or (2) the experimental work being accepted as correct, the tetramethyl derivatives possess the ring which he has assigned (1,5) but there has occurred a ring-shifting during the methylation of at least one of the glycosides. Decision between these alternatives became possible two years later when Wolfrom and Lewis[17] showed that the normal tetramethyl derivatives of glucose and mannose are interconvertible in alkaline solution and that they must consequently possess the same ring. This result left no escape from the conclusion that

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[16] D. H. Brauns, THIS JOURNAL, 45,833 (1923).

[17] M. L. Wolfrom and W. Lee Lewis, *ibid.*, 50, **837** (1928).

the cause of the divergence between the views of Haworth and the writer on ring structures lies in the invalidity of Haworth's assumption that ring-shifts do not occur during the methylation of glycosides.

6. It now became necessary to discard the methylation data that had been used in allocating positions for the rings 1,A and 1,B of the mannose and rhamnose series and to seek the solution of this problem in other ways. It was evident that the ring of the normal methylglucosides, by virtue of the decision that had been reached concerning the true value of the epimeric difference, is 1,B, as was found in the writer's article,[4] but the necessity of discarding methylation data because of the proved ring-shifting left both the 1,4- and 1,5-positions as possibilities for 1,B. How can this question be determined without the use of methylation data? Experimental studies with this object in view have been conducted during the past three to four years by the writer with the assistance of W. C. Austin, J. K. Dale, H. S. Isbell, Edna Montgomery, F. P. Phelps and Clifford B. Purves, to whom grateful acknowledgment of their valuable help is expressed. Their experimental results are published in separate papers. The bearing of these results upon the problem of the ring structures of the sugars will now be discussed.

7. Evidence from the Study of Thiophenol Glycosides.—Purves[18] has confirmed the observation of Fischer and Delbrück[19] that the acid hydrolysis of β-thiophenol lactoside yields galactose and a β-thiophenol glucoside which is identical with normal β-thiophenol glucoside made from acetobromoglucose by the same Koenigs–Knorr synthesis that produces normal β-methylglucoside. He has established the production of the same glucoside from β-thiophenol cellobioside and maltoside by acid hydrolysis. Since the glucose constituent which carries the thiophenyl radical in these disaccharide glycosides is substituted at its Carbon 4 by a second hexose molecule, as shown by Zemplén[20] from data that do not involve methylation, the 1,4-ring for it is excluded and the 1,5-ring is to be chosen for normal thiophenol glucoside and likewise in all probability for the normal methylglucosides. This indicates that the 1,B ring of the rotatory classifications is 1,5. In consequence 1,A is 1,4. One now perceives that since the methylation of normal methylglucoside (1,B = 1,5) yields normal tetramethylglucose (1,5 by Haworth's results), the 1,5 ring in the glucoside does not shift during methylation. It is in the mannose series that the shift occurs, where normal α-methylmannoside (1,A = 1,4) yields normal tetramethylmannose (1,5 by Haworth's results). (See also par. 25.)

8. Evidence from the Study of Ketoses.—The writer[21] inferred some

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[18] Clifford B. Purves, This Journal, 51, 3619, 3627, 3631 (1929).

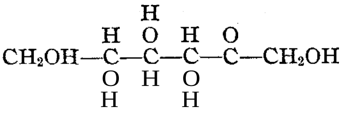
[19] Fischer and Delbrück, *Ber.*, 42, 1476 (1909).

[20] Zemplén, Refs. 11 and 13 and, for the structure of maltose, *ibid.*, 60, 1555 (1927).

[21] Hudson, This Journal, 47, 278 (1925).

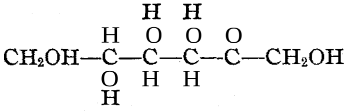
years ago from the value of the difference between the rotation of *l*-sorbose, which does not exhibit mutarotation, and that of α-methyl-*l*-sorboside, that the ketose may persist in solution as its a-form; in such case the absence of mutarotation is to be ascribed to this stability. This view was new and it opened a novel line of inquiry. It has been found subsequently that the development of this idea furnishes a new method of wide applicability for correlating ring structures by comparisons of rotations, as will now be described.

9. Fischer's formulas for the two ketoses that are now named, according to Rosanoff's[22] suggestion, d-sorbose and d-tagatose are (I) and (II). If these are written with rings of the furan type, for example, (III) represents an a-d-sorbose and (IV) an a-d-tagatose. It is seen that (III) and (IV) are modifications of the structure for an α-*d*-xylose (V) and an a-d-lyxose (VI), respectively, of the same ring type, by the substitution of CH_2OH for H. Since the writer[23] has shown that the rules of isorotation apply for β-fructose, β-methylfructoside and the two acetochlorofructoses with the same coefficients that are shown for the aldoses, there is at least considerable probability for the validity of an assumption that the rotation of Carbon 3 (r_3') in the ketoses is the same as that of Carbon 2 (r_2) in the aldoses. These are corresponding carbons because they have like positions with respect to the ring. If this assumption is correct, the value of $2r_3'$ for an appropriate pair of ketoses should be the epimeric difference ($2r_2 = 6700$) of the aldose sugars. The $[\alpha]_D$ value of an a-d-tagatose (m. w. 180) may be calculated from that of the known α-*d*-sorbose[24] (43) by this relation to be (43 −



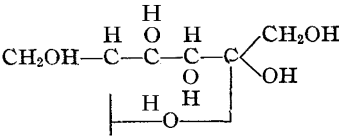
$$CH_2OH-\overset{H}{\underset{\underset{H}{O}}{C}}-\overset{\overset{H}{O}}{\underset{H}{C}}-\overset{H}{\underset{\underset{H}{O}}{C}}-\overset{O}{C}-CH_2OH$$

(I) d-Sorbose

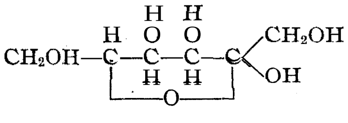


$$CH_2OH-\overset{H}{\underset{\underset{H}{O}}{C}}-\overset{\overset{H}{O}}{\underset{H}{C}}-\overset{\overset{H}{O}}{\underset{H}{C}}-\overset{O}{C}-CH_2OH$$

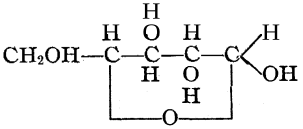
(II) *d*-Tagatose



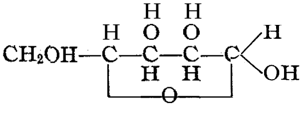
(III) a-d-Sorbose (2,5)



(IV) α-*d*-Tagatose (2,5)



(V) α-*d*-Xylose (1,4)



(VI) α-*d*-Lyxose (1,4)

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[22] Rosanoff, THIS JOURNAL, 28, 114 (1906).

[23] Hudson, *ibid.*, 46, 477 (1924).

[24] In order to make the designation of isomers unmistakable, the $[\alpha]_D$ value will be appended to the names of many substances in this article.

6700/180) = +6°. Tagatose does not exhibit mutarotation[25] and its $[\alpha]_D$ value is +1, which is close enough to the calculated value to warrant the designation of the sugar as *α-d*-tagatose,[26] of the same ring type as *α-d*-sorbose (43), though the position of the common ring is not disclosed because the use of the furan ring in the formulas was arbitrary. Since the assumption regarding Carbon 3 of the ketoses appears justified by the result, one may go a step farther with some confidence and assume that Carbons 4 and 5 of the ketoses have the rotations of the corresponding Carbons 3 and 4 *of the* aldoses. If this assumption is correct, the molecular rotation of *α-d*-tagatose (1 × 180 = 180) should be the same as that of an a-d-lyxose of the same ring type and the $[\alpha]_D$ value of the latter substance can thus be calculated as (1)(180)/150 = 1.2. The rotation of the well-known crystalline lyxose, which is indeed an *α*-form,[27] is +5.5. The agreement is again sufficiently close to warrant the conclusion that a-d-sorbose (+*43*), *α-d*-tagatose (+*1*) and *α-d-lyxose* (+*5.5*) possess a common ring. The allocation of this ring to a definite position will be taken up later in paragraph 16.

10. If the foregoing results (paragraph 9) stood alone, one might be warranted in regarding the theoretical background as speculative and uncertain and the objection might be raised that the rotation of the known form of xylose, a-d-xylose (+92), is far removed from that of its structural relative a-d-sorbose (+43) and that the rotations of @-fructose (−133) and *β-d*-arabinose (−175) also do not show correspondence. But let the argument continue and it will be found that much additional evidence supports the theory. The calculated rotation of that hypothetical a-d-xylose which would have the same ring structure as the known a-d-sorbose is $[\alpha]_D$ = 43(180)/150 = +52. This value in comparison with that of the known a-d-lyxose (5.5) gives a molecular difference (52 − 5.5)150 = 6975 which is quite near the known epimeric difference for sugars (6700), the divergence being less than 2° in specific rotation;[27] the result is clear evidence that the unknown xylose form is the true epimer of the known a-d-lyxose (5.5). It also follows that the known form of a-d-xylose must possess a different ring from that of a-d-lyxose, a-d-sorbose and *α-d*-tagatose. One can surmise that these rings are 1,4 and 1,5, but for the present let the question remain open; it will be considered further in paragraph 16. A similar view in the case of the divergence between the rotations of fructose and arabinose is natural; it will be considered in paragraph 19.

11. In the case of *d*-mannoketoheptose,[28] another ketose which does

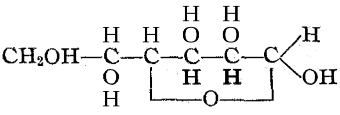
[25] Lobry de Bruyn and van Ekenstein, ***Rec. trav. chim.*, *16*,** 241 (1897).

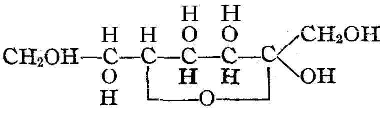
[26] Independent evidence on the question whether crystalline tagatose is an alpha or beta form of the sugar would be obtainable from the preparation of a pure methyltagatoside, as is obvious from the discussion of the similar sorbose example (Ref. 21).

[27] Compare the similar indications made by Phelps and Hudson, THIS JOURNAL, 50, 2050 (1928).

[28] F. B. LaForge, J. *Biol.* ***Chem.*, *28*,** 511 (1917).

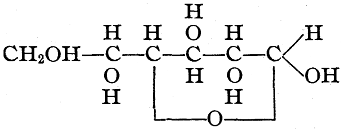
not show mutarotation, its $[\alpha]_D$ value (+29) gives good support to the theory and its ring structure can be definitely allocated. Its configuration (VIII) is like that of d-mannose (VII) and its molecular rotation ((29)(210) = 6090) is so near that of the known α-*d*-mannose[29] ((30)(180) = 5400), which has been shown to possess the 1,A = 1,4 ring (paragraph 7), that one can confidently assign the same ring to this ketose and further designate it as being an alpha form, a-d-mannoketoheptose (2,5).

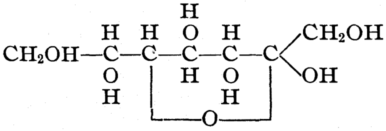

(VII) α-*d*-Mannose **(30)**


(VIII) a-d-Mannoketoheptose (29)

12. The numerical agreements that have been shown in paragraphs 9, 10 and 11 led the writer to believe that the theoretical views which account for them are sound as a first approximation, but it was considered prudent to submit them to a further experimental test before possible publication. The additional evidence which was obtained will now be described.

13. The ketose which would be epimeric with a-d-mannoketoheptose (VIII) would have the structure (X) and would be designated α-*d*-glucoheptulose by recognized custom.[30] Its structure is like that of a-d-glucose (1,A = 1,4) (IX), an unknown form of d-glucose whose rotation was calculated by the writer,[4] through the addition of the epimeric difference to the rotation of a-d-mannose (30), to be $[\alpha]_D$ \$67. Having regard to the molecular weights of the two sugars, the $[\alpha]_D$ value of a-d-glucoheptulose


(IX) a-d-Glucose (1,A = 1,4)


(X) α-*d*-Glucoheptulose (2,5)

(2,5) is calculated to be (67)(180)/210 = \$57. The rotation can also be calculated from that of the known a-d-mannoketoheptose (29), by adding the epimeric difference, as (29 + 6700/210) = +61. Bertrand and Nitzberg[31] have obtained a new crystalline ketoheptose through the oxidation of a-glucoheptitol by the sorbose bacterium and have expressed the view, for which they have adduced considerable experimental evidence, that it is either the d- or the *l*- form of glucoheptulose. Its $[\alpha]_D$ value is

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[29] P. A. Levene, *J. Biol.* Chem., 57,329 (1923); 59,129, 141 (1924).

[30] It seems to the writer that it would be of distinct advantage to adopt for *d*-mannoketoheptose the new name d-mannoheptulose in conformity with the practice of using the ending -ulose (taken from levulose) for ketoses (Bertrand, Wohl and Freudenberg).

[31] Bertrand and Nitzberg, *Compt.* rend., 186, 925 (1928).

-67.5 and mutarotation is not exhibited. If this ketose is truly an a-form of *l*-glucoheptulose, its existence supports the theory, because the rotation of a-d-glucoheptulose must then be $+67.5$, which is near the values given by the two independent calculations. On the contrary, if it is *d*-glucoheptulose or is a *β*-form, no support is given the theory. It appeared necessary, therefore, to synthesize d-glucoheptulose by chemical means in order to decide these questions and the task was undertaken by W. C. Austin. He has synthesized the pure crystalline ketose, found its $[\alpha]_D = +67.5$ in water, without mutarotation, and has prepared a pure crystalline methyl-d-glucoheptuloside from it, the rotation of which ($[\alpha]_D$ $+108.5$) proves that the sugar is an a-form; the results thus support the theory excellently. The method of synthesis was the Lobry de Bruyn rearrangement of *d-α*-glucoheptose in alkaline solution, and Austin's work was much aided through earlier studies by Edna Montgomery, who had synthesized by this rearrangement a new ketose, named lactulose, from lactose and had determined the optimum conditions for the rearrangement and for separating the resulting ketose from its accompanying aldoses. This separation was accomplished by oxidizing the aldoses with bromine water in the presence of barium or calcium benzoate as a buffer, The latter development came in turn from the work of H. S. Isbell.[32]

14. The evidence which has been presented in paragraphs 9–13 correlates the rotations of so many ketoses and aldoses that the essential correctness and usefulness of the theory which has accomplished this result appear established. The next step in logical order would be the allocation of definite ring positions to the forms of lyxose, sorbose, tagatose and xylose that were correlated in paragraphs 9 and 10, but this will be deferred to paragraph 16 in order that Dale's evidence regarding a third form of mannose may be shown in its relationship to the problem of ring structure.

15. Evidence from the Existence of a Third Form of Mannose.—J. K. Dale[33] has isolated a crystalline compound of d-mannose and calcium chloride possessing the composition $C_6H_{12}O_6 \cdot CaCl_2 \cdot 4H_2O$. Its initial rotation corresponds to the value $[\alpha]_D$ -60 for its mannose component. This

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[32] Hudson and Isbell, THIS JOURNAL, 51, 2225 (1929). The synthesis of lactulose was described by Montgomery and Hudson in an address before the National Academy of Sciences at its meeting in Washington in April, 1929, and the paper will be published in the near future. The new ketose was named lactoketose [*Science*, 69, 556 (1929)] but the authors have subsequently decided to name it lactulose. The synthesis of d-glucoheptulose by Austin was announced on the program of the meeting of the American Chemical Society in Minneapolis, Sept. 9–13, 1929, and the paper will be published soon by him. His synthesis of *α*-methyl-*d*-glucoheptuloside, which has been accomplished since his return to his own laboratory, will likewise be published soon. The writer is indebted to Dr. Austin for the kind permission to refer in the present article to his measurement of the rotation of the latter substance and to the resulting proof that the ketose and its methylglycoside are alpha forms.

[33] J. K. Dale, THIS JOURNAL, 51, 2788 (1929).

is closely the rotation which the writer predicted[2] (−65) for β-*d*-mannose of the 1,A ring structure. The discovery of this substance is another link in that long chain of experimental evidence which shows that the two forms of mannose which were previously known, of rotations +30 and −17, possess unlike rings. The rotation of Dale's third form shows that it possesses the ring of a-d-mannose (30) and consequently that the β-*d*-mannose of −17 rotation must be of another ring type because the existence in solution of three forms of the same ring structure cannot be reconciled with the firmly established Le Bel–van't Hoff theory of the asymmetric carbon atom. Since Haworth and Hirst[34] deny the validity of the writer's conclusion from rotatory considerations that the two older forms of mannose do not possess the same ring, the writer replies by referring to Dale's third form of mannose and the significance attached to the magnitude and sign of its rotation.

16. Referring back to paragraphs 9 and 10 there will now be considered the problem of assigning definite ring positions to the known alpha forms of xylose, lyxose, tagatose and sorbose. Xylose is similar to glucose in the configurations of its carbon atoms and lyxose is similar to mannose. It has long been known[2] that lyxose shows certain peculiarities that pertain likewise to mannose and rhamnose. Recently Levene and Wolfrom[35] have synthesized an acetylated methyilyxoside which closely resembles in its peculiar behavior on alkaline de-acetylation those similar derivatives of mannose and rhamnose to which the writer assigned the 1,C = 1,3 ring structure.[2] Both mannose and lyxose are exceptions to the general rule that a monosaccharide aldose yields a mixture of its alpha and beta methylglycosides when heated with acidified methyl alcohol; with these sugars the reaction proceeds nearly quantitatively to α-methylmannoside[36] (79) or lyxoside[37] (59) without the production of a beta isomer, in so far as has been determined. It is natural to surmise from these similarities that *a*-methyllyxoside (59), and therefore a-d-lyxose[2] (5.5), possesses the 1,A = 1,4 ring of a-methylmannoside (79); on this view the other ring 1,B = 1,5 should be assigned to a-d-xylose (92) and its methylxylosides (see paragraph 10). This result would show that crystalline xylose and glucose have the same ring, which seems probable from the fact that their configurations are similar. On the contrary, if the lyxoside is 1,5 the xyloside is 1,4 and the behavior of the pentoses becomes dissimilar to that of the analogous hexoses, which seems improbable. However, this argument is founded only on probabilities concerning chemical behavior and it needs a definite quantitative basis. Data from which the ring assignment can be made

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[34] Haworth and Hirst, J. *Chem. Soc.*, 1221 (1928).

[35] Levene and Wolfrom, J. *Bwl. Chem.*, 78,525 (1928).

[36] Van Ekenstein, *Rec. trav. chim.*, *15*, 223 (1896); Fischer and Beensch, *Ber.*. 29, 2927 (1896).

[37] Phelps and Hudson, THIS JOURNAL, 48, 503 (1926).

with assurance have just recently been published by H. S. Isbell,[38] who has prepared a-methyl-d-guloside ($[\alpha]_D$ +106 in water) and its beta isomer (−83 in water). Since the difference between the molecular rotations (194 (106 − 83) = 36,700) is quite near the usual value for an α,β pair of glycosides (approximately 36,950),[39] there is no doubt that these gulosides possess the same ring, whatever its position may be. Let it be assumed that the ring is 1,B = 1,5. Then we may write the molecular rotations of these d-gulosides as follows, where a„, r_2, r_3, r_4 and r_5 represent the molecular rotations of Carbons 1 to 5 and the signs correspond with the configurations established by Fischer

$$\text{a-Methyl-d-guloside,}\quad a_{„} + r_2 + r_3 - r_4 + r_5 = 20{,}600 \qquad (1)$$
$$\beta\text{-Methyl-}d\text{-guloside,}\quad -a_{\text{me}} + r_2 + r_3 - r_4 + r_5 = -16{,}100 \qquad (2)$$

Applying the rule of optical superposition, we have for the methyl-*d*-glucosides[40] of the same 1,B = 1,5 ring type

$$\alpha\text{-Methyl-}d\text{-glucoside,}\quad a_{„} + r_2 - r_3 + r_4 + r_5 = 30{,}830 \qquad (3)$$
$$\beta\text{-Methyl-}d\text{-glucoside,}\quad -a_{\text{me}} + r_2 - r_3 + r_4 + r_5 = -6{,}630 \qquad (4)$$

The pairs of equations (1), (2) and (3), (4) yield (5) and (6), respectively,

$$r_2 + r_3 - r_4 + r_5 = 2{,}250 \qquad (5)$$
$$r_2 - r_3 + r_4 + r_5 = 12{,}100 \qquad (6)$$

The value of the epimeric difference, $2r_2$ = 6700, gives

$$r_2 = 3{,}350 \qquad (7)$$

Equations (5), (6) and (7) can be transposed to

$$r_2 - r_3 + r_4 = 8{,}275 \qquad (8)$$

If it is assumed that the rules of isorotation hold for the pentoside and hexoside series, Equation 8 represents the molecular rotation of the chain of that pair of methyl-d-xylosides which possesses the 1,B = 1,5 ring structure and the molecular rotations of the alpha and beta members of this pair can be obtained by adding a„ and $-a_{\text{me}}$, respectively, to Equation (8). The value of a„ is taken from the rotations of the known pair of methyl-*d*-

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[38] Isbell, ***Bur.* of *Standards J. of Research,*** December, 1929. Dr. Isbell and the writer collaborated in the large-scale laboratory production of gulonic lactone and it was planned to proceed in the work to the study of derivatives of gulose and the higher carbon aldoses and ketoses obtainable from it. Subsequent to the writer's transfer from the Bureau of Standards to the Hygienic Laboratory in November, 1928, Dr. Isbell continued the project alone. The importance of the experimental results which he has now published is obvious, but the theoretical part of his article appears unsound to the writer because the invalid ring assignments of Haworth have been postulated. An obvious algebraic misstatement in the paper requires correction at once because it concerns the important question whether β-*l*-arabinose (175) possesses the same ring as β-methyl-*l*-arabinoside (245). The required correction is explained in the subsequent paragraph 20 that deals with the arabinose structures.

[39] Hudson, THIS *JOURNAL*, 47, 270 (1925).

[40] The values for the glucosides are taken from the measurements of C. N. Riiber, *Ber.*, 57, 1797 (1924).

xylosides as 17,990,[39] giving for the 1,B = 1,5 methyl-d-xylosides the calculated values

$$\text{a-Form,}\quad a_{\text{me}} + r_2 - r_3 + r_4 = 26{,}265,\ [\alpha]_{\text{D}}\ 160 \qquad (9)$$

$$\beta\text{-Form,}\quad -a_{\text{me}} + r_2 - r_3 + r_4 = -9{,}715,\ [\alpha]_{\text{D}}\ -59 \qquad (10)$$

These values are near the rotations of the known methylxylosides (154 and -65, respectively) but are far removed from those that may be calculated from the application of the epimeric difference to the rotation of a-methyl-d-lyxoside (59), namely, 100 and -119.[41] This result is supported by a similar calculation in which one assumes that the gulosides possess a 1,4-ring; in this case Equations 1, 2, 5 and 7 remain unchanged but the rotations in 3 and 4 become 22,030 and $-15{,}430$, respectively, since these are the values for the methyl-d-glucosides of the 1,A = 1,4 ring form.[4] The solution now yields for the a-form of methyl-d-xyloside (1,4) the $[\alpha]_{\text{D}}$ value 133 and for the β-form -86; these calculated values are so widely divergent from those of the known methylxylosides (154 and -65) and also from those of the other expected forms mentioned above (100 and -119) that the original assumption of a 1,4-ring for the methylgulosides must be discarded. These two calculations thus show that the known methylxylosides and gulosides possess the 1,5-ring of the glucosides. Combining this result with the conclusions of paragraphs 9 and 10, it is seen that the 1,A = 1,4 ring pertains to α-*d*-lyxose (5.5), a-d-sorbose (43) and α-*d*-tagatose (1), and it is interesting to observe that this ring has now been allocated to the known forms of the four non-mutarotating ketoses (sorbose, tagatose, mannoketoheptose and glucoheptulose) and that all these sugars are alpha forms. Lastly, it is mentioned that the correlations which are shown in this paragraph are based upon the assumption that the isorotation rules hold between the pentoside and hexoside series; this is the further independent evidence that was mentioned in paragraph 3, footnote 10, as forthcoming in support of the writer's assumption[4] that r_4 has the same value in the pentoside and hexoside series.

17. The ring structure of the known form of *d*-α-glucoheptose[42]

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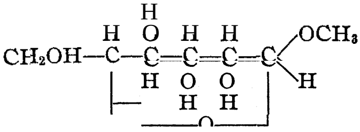
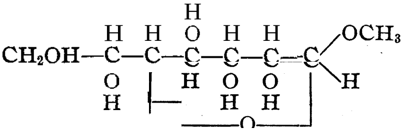
[41] Ref. 27. The value for the levorotary form is obtained by subtracting the difference in specific rotation of the known methylxylosides (219) from the calculated rotation (100) of the dextrorotary form. It is evident from consideration of paragraph 10 that the xylosides of rotations 100 and -119 belong to the unknown form of xylose that has the same ring structure as a-methyl-d-lyxoside (59).

[42] Fischer's designation of the two d-glucoheptoses, which are distinct sugars, by the symbols a and β was expressly stated by him to be provisional in the lack of a better plan *[Ann.,*270, 64 (1892)]. The subsequent use of these letters to designate a pair of forms of a sugar or its glycosides, such as ***a***- and p-glucose, ***a***- and β-methylglucoside, etc, has become universal. In consequence there is considerable chance for confusion today when we must refer to the known form of a-glucoheptose (a beta modification) as β-*d*-α-glucoheptose. The writer is strongly in favor of adopting some new system for naming the higher carbon sugars in order that the terms α and β may be restricted

can be found from the allocation that has been made for the 1,5-ring in the methylgulosides. Referring to the structures (XI) and (XII), it is seen that



(XI) β-Methyl-*d*-guloside (—83).



(XII) β-Methyl-*d*-α-glucoheptoside[43] (−75)

the observed molecular rotations [(—83)(194) = −16,100 and (−75)(224) = −16,700] are so closely alike that one may ascribe the same ring to the two substances, provided the rotation of Carbon 6 in the heptoside is negligible. That this is the case is indicated by the results that were found some years ago in comparing several substances from the galactose and mannoheptose series.[44] In paragraph 16 it was shown that the ring of the guloside is 1,B = 1,5, hence this is the structure of the glucoheptoside and of the known beta[39] form of d-a-glucoheptose (—28). The data indicate that the determination of ring structures in the heptose series through comparison with the allocations in the hexose series will be a comparatively simple matter and it may be surmised that this remark will apply also to the octoses and higher monosaccharides.

18. It will next be shown that the rotation of a new form of lyxose recently discovered by Haworth and Hirst,[34] which they have designated β-*d*-lyxose ([α]$_D$ —70), fits accurately in the writer's system of ring classifications. It has been indicated[27] that the [α]$_D$ value for an unknown α-*d*-lyxose epirneric with the known a-d-xylose (92) may be calculated to be (92 − 6700/150) = 47. The ring of this epimeric pair is 1,B = 1,5 (paragraph 16). The rotation of the corresponding β-*d*-lyxose (1,B) may be obtained from the last value by subtracting the difference between the rotations of an a- and β-form of a sugar[45] ($2a_{OH}$ = 16,900 for glucose, corresponding to 16,900/150 = 113 in the [α]$_D$ value of a pentose) and it is [α]$_D$ 47 − 113 = —66, which shows that the new form of lyxose (—70) is β-*d*-lyxose (1,B = 1,5). Since Haworth and Hirst have regarded their discovery of this sugar as an experimental proof that the writer's ring classifications are incorrect, reply is here made by calling attention to this excellent agreement of its rotation with his views.

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in the sugar group to the names of different forms of single sugars, their glycosides, etc. In order that any new system of nomenclature for these higher sugars may receive the general support of research workers in the carbohydrate field, it is believed best to have the subject discussed first by correspondence. The writer plans therefore to send out a circular letter on this subject soon to many workers and it is courteously requested that the possible publication of proposals by individuals be not made while the effort to obtain general agreement is in progress.

[43] Fischer, *Ber.*, 28, 1145 (1895).

[44] Hudson and Monroe. THIS JOURNAL, 46, 979 (1924).

[45] Hudson and Yanovsky, *ibid.*, 39, 1013 (1917).

19. Substances of the arabinose, galactose and fructose series will now be considered. These sugars are related structurally in the same way as the members of the trio xylose, glucose and sorbose or lyxose, mannose and tagatose, and the following comparisons (Table II) apply according to the rules of isorotation. It is seen that the first, fourth and fifth pairs give agreeing rotations for Carbon 4, but that pairs two and three yield very different values. The occurrence of the three agreements leads the writer to believe that substances of like ring structure are represented in pairs one, four and five and this view is supported by the occurrence of the greatly divergent values for pairs two and three. These comparisons thus indicate that the known methyl-1-arabinosides (17.3 and 245.5) have the 1,B = 1,5 ring, but that the **1,A** = 1,4 ring is possessed by the known methyl-*d*-galactosides (192.7 and 0.4) and β-methyl-*d*-fructoside (−172.1). Since the known a- and β-forms of d-galactose (144 and 52) possess the same ring as these galactosides, and β-fructose (−133) the same ring as this fructoside,[21] the **1,A** = 1,4 ring pertains to the known forms of these sugars. The rotation of the only known form of Larabinose (175) differs from that of β-methyl-*l*-arabinoside (245) by **a** value that has been shown[21] to be abnormal, and in consequence the writer leaves the question of its ring form undecided and awaits the production of new experimental evidence regarding this point. It is interesting to observe from pairs one, four and five of the table that ***the*** rotation of Carbon 4 ***has*** concordant values for ***the*** *1,4-* and *1,5-ring* structures. This new result appears to offer explanation for the fact that while the original comparisons4 of the writer, which led to the

TABLE II

RING INDICATIONS FOR THE ARABINOSE, GALACTOSE AND FRUCTOSE SERIES

Substance	$[M]_D$	Rotation of Carbon 4 **(Difference /2)**
β-Methyl-*l*-arabinoside	40,300	7,550
a-Methyl-d-xyloside (1,5)	25,200	
β-Methyl-*l*-arabinoside	40,300	11.930
a-Methyl-d-xyloside (1,4)	16,440[46]	
a-Methyl-d-galadoside	37,380	3,275
a-Methyl-d-glucoside (1.5)	30,830	
α-Methyl-*d*-galactoside	37,380	7,675
a-Methyl-d-glucoside (1,4)	22,030[47]	
β-Methyl-*l*-fructoside	33,400	8,100"
a-Methyl-d-sorboside (1,4)	17,200	

[a] This value applies to Carbon 5 of the ketosides, which is the analog of Carbon 4 of the aldosides (paragraph 9).

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[46] This value is calculated from that of the known a-methyl-d-lyxoside (59.4) by use of the epimeric difference (6700).

[47] This value is calculated from that of the known α-methyl-*d*-mannoside (79) by use of the epimeric difference.

conclusion that an unknown form of a-methyl-d-glucoside of $[\alpha]_D$ 115 may be expected, were based upon the evidence from methylation data that the known methylxylosides, arabinosides and galactosides are 1,5-forms and this evidence is now apparently invalid in the case of the galactosides, the comparison gave a correct result even though its theoretical background is now seen to have been formally defective. It yielded a correct result because essentially the same value for the rotation of Carbon 4 pertains to the 1,4- and the 1,5-ring structures.

20. The writer's original comparisons[4] of the rotations of the methyl glucosides, galactosides, xylosides and arabinosides, discussed in the preceding paragraph, will now be modified in Table III through the use of the new ring assignments of the present article, so that they may obtain a proper theoretical .basis. The symbols are the ones originally used.

TABLE III

DERIVATION OF THE ROTATIONS OF *α*-METHYL-*d*-GALACTOSIDE (1,5) AND *β*-METHYL-*l*-ARABINOSIDE (1,4)

Substance	Molecular rotation	
β-Methyl-*l*-arabinoside (1,5)	$r_4 + p = 40{,}300$	(11)
a-Methyl-d-xyloside (1,5)	$-r_4 + p = 25{,}200$	(12)
a-Methyl-d-galactoside (1,5)	$r_4 + p' = X$	(13)
a-Methyl-d-glucoside (1,5)	$-r_4 + p' = 30{,}830$	(14)
β-Methyl-*l*-arabinoside (1,4)	$r_4' + p'' = Y$	(15)
a-Methyl-d-xyloside (1,4)	$-r_4' + p'' = 16{,}440$[46]	(16)
a-Methyl-d-galactoside (1,4)	$r_4' + p''' = 37{,}380$	(17)
α-Methyl-*d*-glucoside (1,4)	$-r_4' + p''' = 22{,}030$[47]	(18)

Solving Equations 11 to 14 gives the $[\alpha]_D$ value **237** for the unknown *α*-methyl-d-galactoside (1,5) and Equations 15 to 18 lead to 193 as the $[\alpha]_D$ value of the unknown *β*-methyl-*l*-arabinoside (1,4). It is thus to be expected that the unknown 1,5-methylgalactosides will be more dextrorotatory than the known 1,4-forms and the same conclusion follows for the corresponding forms of galactose of the 1,5-ring type; an a-d-galactose (1,5), of greater dextrorotation than the known 1,4 a-form (144) is thus predicted. In the arabinose series the unknown *β*-*l*-arabinose (1,4) would be expected to have the $[\alpha]_D$ value[48] $[(193)(164) - (a_{\mathrm{me}} - a_{\mathrm{OH}})]/150 =$ 144, approximately. The question whether these predictions are correct is a subject for future experimental study, but it will be shown in the following paragraph that there is at least some evidence now known which supports them.

21. In 1917 Dr. E. Yanovsky and the writer made several precise measurements of the mutarotation curves for *α*-*d*-galactose and *β*-*l*-arabinose in water at 20°, seeking especially to follow the change in its early stages. The first readings were made one minute after solution of the

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[48] Ref, 21. The value of a, $-\ a_{\mathrm{OH}}$ was there shown to be about 10,000.

sugar. In the case of both sugars these curves gave coefficients from the unimolecular formula which progressively decreased during the mutarotation. The value for galactose in the early stages was 0.014, expressed in minutes and decimal logarithms, and decreased to 0.0087, a relatively large change; the similar values for arabinose were 0.042 in the early stages and 0.034 toward the end. The initial $[\alpha]_D$ value for arabinose, obtained by extrapolation through the first minute, was +186, which is considerably higher than the value usually accepted for this sugar, 175. Due to interruptions caused by war the subject was not studied further and the results were never published. It is now seen that they throw much light on the possible existence of new forms of galactose and arabinose, and it is planned to publish them soon, together with measurements of the mutarotation of two tetra-acetates of galactose which were performed in the same period. The indication that the initial rotation of β-*l*-arabinose may be considerably higher than 175 throws much light on the question[21] of the supposed anomalous difference between this rotation and that of β-methyl-*l*-arabinoside (245), as it was shown that a„ $- a_{OH}$ has an unusually large value for this pair if the rotation of 175 is assigned to arabinose. The experiments indicate that this value may be much too low. The calculations of Isbell[38] by which he has sought to explain the exceptional value (175) of the rotation of arabinose constitute reasoning in a circle. He has set up a series of simultaneous equations just sufficient in number to allow the determination of the unknown variables, has assumed, of course, that the unknowns have constant values in the set and has solved the equations to obtain these values. Then he has used the values so obtained and found that the difference of two of them (*a*„ $- a_{OH}$) is a constant throughout the set of equations. His conclusion that he has explained the writer's observation regarding the unusual rotation of arabinose is clearly invalid because all that he has done is to check the computations that he made in solving the equations.

22. Similar Sugars.—The writer has long had in mind the idea that it may be possible in time to correlate the physical and chemical properties of sugars with their configurations. The first step toward this goal was the correlation of α- and β-forms in the group. It was then seen[2] that the occurrence in the mannose, rhamnose and lyxose series of forms with various types of ring structure presented a second problem which it is necessary to solve before a comprehensive comparison can be made. The writer believes that the problem of ring structures has now been solved for the greater number of the monosaccharides and that the extension of the solution along the present lines to the remaining simple sugars should offer no obstacles, though the obtaining of the necessary experimental measurements of rotations may require much time. The present results do comprise, however, a sufficiently large number of ring structure determinations to permit the logical comparison of the physical and chemical properties of substances of known configuration and ring structure. These comparisons will be presented in a forthcoming article but it may be mentioned here that the configurations for Carbons 1, 2, 3, 4 and 5 are the principal factors that determine the physical and chemical properties of a monosaccharide. Each of these configurations greatly influences the properties. In the heptoses and higher-carbon monosaccharides the configurations of Carbons 6, 7, etc., have a very minor influence. The writer cannot agree with Drew and Haworth[10] that their comparisons of the rotations of various hexoses and higher carbon monosaccharides constitute evidence for the occurrence of 1,5-rings in the normal forms of all these sugars; his objection arises from the fact that Drew and Haworth have compared the properties of only a few *types* of sugars, although the number of sugars which they have included is large. If other types are considered, their conclusion becomes invalid, as will be shown in detail in the forthcoming article.[49]

23. Haworth and Hirst[34] have criticized the writer's view that the two forms of mannose (30 and −17) differ from each other in ring structure while the alpha and beta forms of glucose (113 and 19) do not, by a statement to the effect that if the historical order of events had been different and the forms of mannose had been discovered before those of glucose, the writer would now be assuming that the mannose forms possess a like ring and the glucose modifications different ones. The writer requests to be excused from the task of considering an altered historical order for the origin of ideas in science; the subject is too complex for portrayal or even for precise definition. Instead, he will put the question raised by Haworth and Hirst in a form that is suitable for scientific discussion and then make his reply. *Does conclusive evidence exist today that the forms of glucose (113 and 19), rather than those of mannose (30 and −17), give the true difference of rotation for alpha and beta structures of the same ring type?* The answer is in the affirmative. Zemplén's proof[13] that lactose is 4-galactosidoglucose excludes the 1,4-ring for the glucose constituent of this disaccharide and limits the alpha and beta forms of lactose to one type (1,5) of ring structure. The writer showed[3] in 1909 that the difference of their molecu-

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[49] In H. S. Isbell's recent article (Ref. 38) he states that the synthesis of many substances in the hexose group is planned in order to obtain further data for studying the question of ring structures. Since this appears to be notice of the reservation of a part of the experimental field of study in which the writer has been working for twenty years it becomes necessary to record that he was not consulted by Dr. Isbell before this broad statement was made. It is true that Dr. Isbell made an arrangement with the writer for undertaking the pertinent studies in the idose series but the agreement did not include the whole hexose group. While the writer will be much pleased to have other workers undertake the preparation of substances that are needed for the extension of these ring classifications and will gladly make proper arrangements upon request, he obviously must object to Dr. Isbell's unwarranted assumption of the right to reserve a portion of this field against him.

lar rotations has essentially the same value as is found for the forms of glucose; it is thus established that the correct value for the rotation difference is found in the glucose rather than in the mannose series. Corroboration of this evidence can be obtained through similar reasoning by combining (1) the observation that the alpha and beta acetates of glucose, lactose, cellobiose and maltose show a uniform difference of molecular rotation,[50] with (2) Zemplén's proof[20] that each of these disaccharides is a 4-hexosido-glucose.

24. The ring structures that have been disclosed in this article cannot be reconciled with an idea that has become current from various publications by Haworth, who maintains that glycosides which possess the furan ring are very readily hydrolyzed. The furan-ringed methylglycosides, such as a-methylmannoside (79), a-methyllyxoside (59) and β-methylfructoside (-172) are quite comparable with the normal methylglycosides of the 1,5-ring in resistance to acid hydrolysis. In the writer's opinion the very easily hydrolyzed glycosides, of the type of Fischer's third methylglucoside, possess neither the 1,4- nor the 1,5-ring but rather the $1,C = 1,3$ ring that has been assigned[2] to those peculiar acetylated methylglycosides of the rhamnose, mannose and lyxose[35] series which hold one acetyl group so firmly bound that it is not removable by alkali. Haworth's experimental results from the study of the methylation of the readily hydrolyzable so-called gamma glycosides, which have led him to regard the methylated products as possessing the furan ring, can be accounted for on the view that the original 1,3-ring has shifted during the methylation. *From this viewpoint the property of being readily hydrolyzed is a strong indication of the presence of a propylene oxide ring and on these grounds the writer would assign this ring to the fructose constituent of sucrose.* It is obvious that the whole system of butylene oxide structures that Haworth has proposed for sugars and glycosides of the so-called gamma type must be revised and reconstructed from evidence that avoids the invalid assumption of ring stability during methylation. This assumption is likewise present in all of Haworth's ring allocations among the compound sugars and this subject must likewise be reopened. In the following article the writer will endeavor to show that ring allocations for the compound sugars can be made through the use of the rules of isorotation and that the results indicate that ring shifting during the methylation of several of the compound sugars has occurred in Haworth's experimentation.

25. **Postscript of January** 13, 1930.—After this article was sent in for publication, the writer noticed the observation of Fischer and Armstrong,[51] made 29 years ago, that normal β-methylglucoside is produced from β-methylmaltoside by the hydrolytic action of the enzymes present in yeast.

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[50] Hudson and Dale, THIS JOURNAL, 40,993 (1918).

[51] Fischer and Armstrong, *Ber.*, 34, 2885 (1901).

It will be seen on reference to paragraph 7, that this observation proves that β-methylglucoside cannot possess the 1,4-ring, and must therefore be assigned the 1,5-ring. The old observation falls quite in line with the views which have come from the study of the thiophenol glycosides of lactose, cellobiose and maltose and Zemplén's proof that the disaccharide linkages are at Carbon 4 in these sugars. Referring to paragraph 16, it will be observed that it is possible to calculate the rotations of the unknown methyl-d-gulosides of the 1,A = 1,4 ring from the molecular rotations of the methyl-d-glucosides (1,A = 1,4), the methyl-d-xylosides (1,A = 1,4) and the epimeric difference ($2r_2 = 6700$). The appropriate equations are similar to those already recorded and the details may be omitted; the solution yields for a-methyl-d-guloside (1,A = 1,4) the $[\alpha]_D$ value +164 and for the β-form —29. These gulosides are now unknown. It is obvious that the rotations of a very large number of other glycosides and sugars, both aldoses and ketoses, of the pentose, hexose and heptose series and of the 1,4- and 1,5-ring structures may now be calculated from existing data by the rules of optical superposition and isorotation. The rotations of the individual asymmetric carbon atoms in these substances can likewise now be obtained; the values are of course quite different from the erroneous ones that Isbell[38] has recently published for the pentose and hexose series. He has fallen into the error of Haworth and has neglected to examine the fundamental assumption regarding ring stability during methylation, with the result that he has assigned incorrect rings to many substances. The writer would prefer to postpone the publication of the very obvious calculations of the rotations of the individual carbon atoms until the question of the ring structures in the galactose, arabinose and fructose series becomes definitely settled and he hopes that others will not burden the literature with such calculations while the subject still involves some possible uncertainties.

26. Postscript of January 16, 1930. The Ethyl Glucosides of the 1,A = 1,4 Ring Type Recently Isolated by Haworth and Porter.—It is stated by the authors[52] in their December, 1929, article, which has just come to hand, that the observed rotations of these compounds ($[\alpha]_D$ 98 for the a-form and —86 for the β) disprove the writer's views on ring structure and the "epimeric difference of rotation" as expressed in his 1926 articles. The writer disputes this conclusion and maintains on the contrary that the isolation of these substances of the observed rotations is a striking experimental confirmation of his prediction of the rotations in the glucose (1,A) series from the epimeric difference as applied to the substances of the mannose (1,A) series. The reading of the present article, in which it is shown (paragraphs 4–7) that the writer's acceptance of methylation data in his 1926 work led to the erroneous assignment of the 1,5-ring to the 1,A substances whereas the discarding of such data now leads to the assignment

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[52] Haworth and Porter, J. Chem. *Soc.*, 2796 (1929).

of the 1,4-ring to these compounds, clears up in full the objections which Haworth and Porter have made and shows that their latest results confirm the writer's ring system and do not agree, as regards the mannose series, with their own assignments of ring structure nor with Haworth's assumption that ring shifts never occur during the methylation of glycosides. It will now be shown that the rotations of the new ethylglucosides correspond with the values that the writer calculated in 1926 for the analogous methylglucosides of the 1,A ring, which is shown in the present article to be the 1,4-ring. Since the value of a,, — a, is approximately 1000,[21] the specific rotations of the ethyl-d-glucosides (1,A = 1,4) (mol. wt. 208) may be obtained from the rotations of the methyl-d-glucosides (1,A = 1,4) (mol. wt. 194) that were calculated in the 1926 articles ($[\alpha]_D$ 114 for the a-form and —77 for the β) as follows

α-Ethyl-*d*-glucoside (1,A = 1,4), $[\alpha]_D = [(114)(194) + 1000]/208 = 111$

β-Ethyl-*d*-glucoside (1,A = 1,4), $[\alpha]_D = [(-77)(194) - 1000]/208 = -77$

These calculated values indicate quite clearly that the new substances of Haworth and Porter may well be the ethylglucosides of the 1,4-ring, as they contend; the rotations fall in with the writer's system of ring structures but they prove at the same time, through the epimeric difference, that a-methyl-d-mannoside (79) possesses the 1,4-ring likewise, as contended by the writer, and not the 1,5-ring that has been assigned by Haworth to the latter substance. The difference of 9–13 between the calculated and observed values for the new ethylglucosides is not large enough to show conflict with the writer's views; such moderate differences are readily accounted for when it is remembered that the isorotation rules are in reality only first approximations, though it is known that they hold for sugars and alkylglycosides far within the limits by which substances of different ring structure vary in rotation. In connection with the new ethylglucosides it should be mentioned that Haworth and Porter find them to be very easily hydrolyzed by acids; if this is a fact and if they are really the expected 1,4-glucosides, the writer regards the observation as evidence that the ease of hydrolysis of glycosides is not conditioned solely by the type of ring that is present but that other structural elements are also of influence. It may be necessary to accumulate much additional experimental evidence on this question before definite correlations between structure and relative ease of hydrolysis can be made on a sound basis, and some of the reasoning of paragraph 24 may be affected by such new data. It is possible also that the same view may apply regarding the ease of oxidation of sugars of different ring structures by permanganate; who can say that because glucose of the 1,4-ring may be more easily oxidized than glucose of the 1,5-ring that the same correlation applies to a sugar of another configuration, for example galactose, mannose or fructose? Such questions as these, regarding which very definite assumptions applying throughout the sugar group have been made by Haworth, can be decided by experiment alone and the necessary data do not now exist.

27. Summary

It is shown that the measurements of Brauns on the aceto-halogeno derivatives of cellobiose and 4-glucosidomannose, taken in conjunction with the proof by Wolfrom and Lewis that normal tetramethylglucose and normal tetramethylmannose are true epimers, disprove Haworth's assumption that rings never shift during the methylation of glycosides. In consequence the whole system of ring structures which Haworth has built up for the simple and compound sugars, which is based upon this assumption, loses its foundation and the questions must be restudied through the use of evidence which avoids this invalid assumption. Such evidence is presented and the ring structures of many of the monosaccharides are disclosed through the application of the rules of optical superposition and isorotation.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

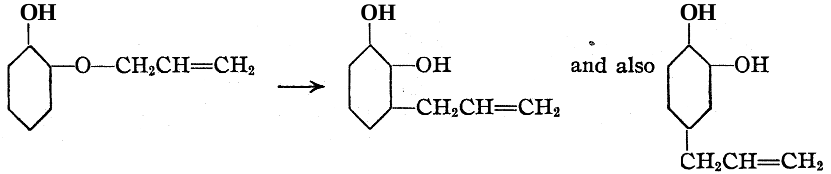
THE BEHAVIOR OF ALLYL DERIVATIVES OF CATECHOL AND RESORCINOL TOWARD HEAT

BY CHARLES D. HURD, HARRY GREENGARD AND FORREST D. PILGRIM

RECEIVED JANUARY 10, 1930 PUBLISHED APRIL 7, 1930

Except in a few instances, study of the pyrolytic rearrangement of allyl aryl ethers[1] has been confined to derivatives of monohydric phenols. In many such cases it has been observed that the allyl group wanders to an ortho carbon of the aromatic nucleus, thereby forming an o-allyl-phenol, unless both ortho positions are previously substituted, in which case the rearrangement proceeds normally to the para position.

Similar experiments with dihydric phenols have been little studied. In fact, when these experiments were undertaken in 1926 no work whatsoever had been published in this field. Two articles[2] have since appeared dealing with the mono- and diallyl ethers of catechol. The former has been shown to rearrange into both 3-allylcatechol and 4-allylcatechol, the former predominating.



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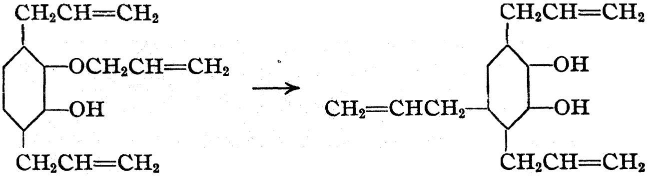
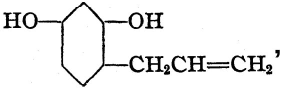
[1] For a survey of this topic, see Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., New York, 1929, pp. 214–228.

[2] Kawai, *Sci. Papers Inst. Phys. Chem. Res.*, 3, 263 (1926); Perkin, Jr., and Trikojus, *J. Chem. Soc.*, 1663 (1927).

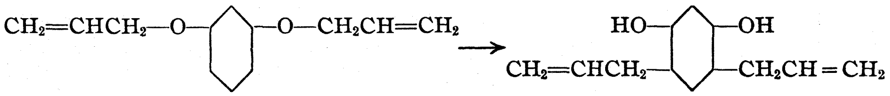
From the diallyl ether, Kawai obtained evidence for rearrangement into 3,5-diallylcatechol. Our work has included a similar study of these ethers and in addition several other allylcatechols have been synthesized and studied. Triallylcatechol was obtained in two ways: first, from the rearrangement of the monoallyl ether of diallylcatechol



and, second, from the diallyl ether of monoallylcatechol. Tetra-allylcatechol was prepared by heating the diallyl ether of diallylcatechol.

Allyl Ethers of **Resorcinol.**—The monoallyl ether of resorcinol offers the interesting possibility of "ortho" rearrangement into either 1-allyl-2,4-dihydroxybenzene or 2-allyl-1,3-dihydroxybenzene, but only the former, , appears to be formed. This was confirmed by methylation and oxidation into 2,4-dimethoxybenzoic acid. Several attempts were made to oxidize the allyl-dimethoxy-benzene directly but all met with failure.[3] This oxidation was readily accomplished, however, by converting the allylresorcinol first into either propenylresorcinol or its dimethyl ether, $(CH_3O)_2C_6H_3CH{=}CHCH_3$, by heating with alkali. The last compound oxidized readily to 2,4-dimethoxybenzoic acid, the melting point of which was found to agree with the recorded value[4] of 108". The alternative isomer, 2,6-dimethoxybenzoic acid, was clearly excluded by its high m. p.,[5] 179".

Similarly, the diallyl ether of resorcinol[6] was found to undergo rearrangement at 210° into 1,5-diallyl-2,4-dihydroxybenzene



The diallyl ether of the latter compound still has two available nuclear carbon atoms, but one of them is meta. Therefore, it would be anticipated that but one of the allyl groups should be affected by the heating.

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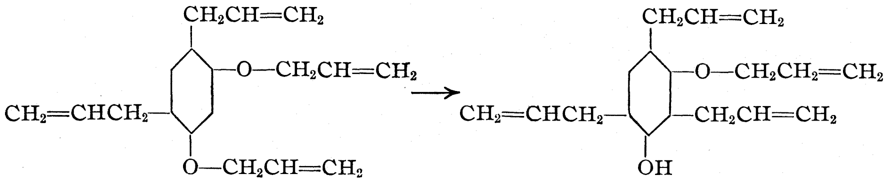
[3] Some of these trials were carried out by Mr. D. H. McQueen.

[4] Tiemann and Parrisius, *Ber.*, 13, 2378 (1880); von Pechmann and Duisberg, *ibid.*, 16, 2126 (1883).

[5] De Bruyn, *Rec. trav. chim.*, 2, 222 (1883).

[6] Wilson and Adams, THIS JOURNAL, 45, 533 (1923), prepared the diallyl ether of resorcinol, $m\text{-}C_6H_4(OCH_2CH{=}CH_2)_2$, from resorcinol-*bis*-(γ-bromopropyl) ether, $m\text{-}C_6H_4(OCH_2CH_2CH_2Br)_2$, by heating the latter to 225°. Some rearrangement of the diallyl ether into a diallylresorcinol may have occurred during this synthesis because of the high temperature, but this possibility seems not to have been studied.



It was definitely established that such was the case by proving that the resulting compound possessed but one hydroxy group and not two, by means of the phenyl isocyanate derivative.

Experimental Part

Monoallyl Ether of Resorcinol.—Only the preparation of this ether will be described in detail, but the general method of preparation for the others will be outlined.

Molar quantities of potassium carbonate and resorcinol were mixed in 200 cc. of acetone, with some evolution of heat. The flask containing this mixture was then fitted with a stirrer and attached to a reflux condenser. A mole of allyl bromide was added slowly and with constant stirring. When about three-fourths of it had been added, external cooling of the flask was necessary to prevent too vigorous boiling. The remaining allyl bromide was added with less evolution of heat. Refluxing on a water-bath with continual stirring was continued for four hours. After cooling, the solid material was filtered off and washed with 50 cc. of acetone. The washings were added to the first filtrate and the acetone was removed by distillation. A test portion of the residual oil was placed in a few cc. of sodium hydroxide solution. Since it seemed to dissolve completely, this demonstrated the absence of any great amount of the diallyl ether. The oil was then fractionally distilled, and the portion coming over up to 122" at 2 mm. was collected; yield, 112.5 g. On redistillation, the main portion came over at 106–110° and 3 mm. A small portion (5 g.) of the diallyl ether was collected above 135".

Analysis of the 106–110° (3 mm.) liquid for hydroxyl group with methylmagnesium iodide by the Zerewitinoff method revealed the presence of considerable resorcinol. In fact, resorcinol crystallized out of this distillate (and of other similar distillates) after a few days' standing. This admixed resorcinol was removed by shaking the mass with water. A little hydrochloric acid was found to be useful in breaking the emulsion thus produced. After drying over sodium sulfate, the pure monoallyl ether of resorcinol was then distilled. These physical constants were obtained: b. p. 122° at 2 mm.; 133° at 6 mm.; 141° at 33 mm.; n_{D}^{15} 1.5525; n_{D}^{30} 1.5474. Analysis of this material for hydroxyl indicated at least 99% purity. The yield of this purified material, based on the original resorcinol taken, was 27–30%.

Anal. (Zerewitinoff). Subs., 0.1820: CH4 evolved, 0.0200 g. Calcd. wt. of CH4 to be evolved from $HO\text{-}C_6H_4\text{-}OC_3H_5$, 0.0194.

Although the monoallyl ether of resorcinol distils as a colorless oil, it darkens considerably if it is kept bottled for two or three weeks.

General Method of Preparation of the Allyl Ethers.—In general, the catechol or resorcinol was refluxed[7] for four to five hours in acetone solution with the calculated quantity of allyl bromide and with a slight excess of fused potassium carbonate. For

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[7] This period of refluxing was necessary for good yields even where there was a considerable heat of reaction at the outset. With resorcinol, for example, a 46% yield of the diallyl ether was attained in fifteen minutes, as compared to an 83% yield in five hours.

convenience in working up the products, a minimum volume of acetone was usually taken. Ordinarily the weight of the catechol or resorcinol compound exceeded the weight of the solvent used. At the termination of the reflux period the mixture was diluted with three or four times its weight of water, the layer of oil which separated was removed, and the aqueous layer thrice ether-extracted. In the case of the diallyl ethers the combined extracts were twice washed with dilute alkali solution (5% sodium hydroxide) and then with water. After drying over anhydrous sodium sulfate or potassium carbonate, the ether was removed and the residual material fractionated in *vacuo*. For the monoallyl ethers this procedure was performed in the manner outlined above for the monoallyl ether of resorcinol. Purification by vacuum distillation was frequently impossible, because of prior rearrangement. In such cases the rearranged product was purified instead. The monoallyl ethers gave the characteristic color reactions with ferric chloride solution. They yielded no precipitate with lead acetate solution in acetone. The diallyl ethers formed no salts and gave no coloration with ferric chloride. A summary of results is given in Table I.

TABLE I

PREPARATION OF VARIOUS ALLYL ETHERS

Original subs. taken	Weight g.	Allyl ether formed	Yield g.	%	B. p., °C. (mm.)
Catechol	22	Mono	17	70	108–113 (18)
Catechol	11	Di[a]	14–18	70–93	130–135 (18); 125–128 (10)
3-Allylcatechol	6	Mono	Rearranged during purification		
3-Allylcatechol	6	Di	Rearranged during purification		
3,6-Diallylcatechol	12	Di	8	47	180–185 (22) some dec.
Resorcinol	110	Mono[b]	38	27	122 (2); 133 (6); 141 (33)
Resorcinol	11	Di	14–16	75–83	149–153 (4); 160–165 (24)
4,6-Diallylresorcinol	11	Di	Rearranged during purification		

[a] Colorless, but turned yellow on standing. The ether possessed a penetrating, irritating odor. [b] Colorless, but darkened (brown) in two weeks. Similar irritating odor.

Pyrolysis of the Allyl Ethers of Catechol, Resorcinol and their Analogs. Properties of the Allylcatechols and of the Allylresorcinols.—In general it was only necessary to heat the allyl ethers to 175–210° (bath temperature) for rearrangement to occur. The reaction completed itself in a short time and in many cases was decidedly exothermic. The red color of the rearranged mass was characteristic. Furthermore, the original sharp allyl ether odor was replaced by a phenol-like odor. Purification was by vacuum distillation.

In all except one case, namely, the diallyl ether of diallylresorcinol, it was shown that both allyl groups in the diallyl ethers wandered from oxygen to a carbon of the aromatic nucleus. Every rearrangement product in the catechol series gave an intense color reaction with ferric chloride, and gave a characteristic gray precipitate with an ammoniacal solution of calcium chloride. Starting with an acetone solution of each of the catechol compounds, the lead salts were readily prepared by precipitation with lead acetate (in acetone solution, 33%).

For an analysis of the lead salts, the sample (0.2–0.5 g.) was washed first with acetone, then with water, dried to constant weight at 105° and then dissolved (pink solution) with 25 cc. of **25%** acetic acid. To this, while hot, was added **3** cc. of concd. sulfuric acid in **10** cc. of water. The mixture was boiled for a short time to coagulate the lead sulfate, which was then collected and weighed.

Similarly, the rearranged products in the resorcinol series gave strong ferric chloride color reactions. The identity of each product of rearrangement was proved by analysis. Certain reactions which are mentioned below were carried out to supply evidence regarding the orientation of the allyl groups in the rearrangement. Details will be supplied only in one case, namely, the pyrolysis of the monoallyl ether of resorcinol. Others will be summarized in Table II.

TABLE II

PYROLYSIS OF ALLYL ETHERS OF CATECHOL AND RESORCINOL COMPOUNDS, TEMPERATURES AND PRODUCTS

No.	Ether heated	Temperature of rearrangement	Product
1	Catechol monoallyl	170–175°, exothermic	3-Allyl- and 4-allylcatechol
3	Catechol diallyl	180°, vig. exotherm.	3,6-Diallylcatechol
5	3-Allylcatechol monoallyl	[a]	3,6-Diallylcatechol
6	3-Allylcatechol diallyl		Triallylcatechol
8	Diallylcatechol diallyl	180–200°	Tetra-allylcatechol
10	Resorcinol monoallyl	210–220°, exotherm.	4-Allylresorcinol[b]
11	Resorcinol diallyl	210°, mod. heat ev.	4,6-Diallylresorcinol
12	Diallylresorcinol diallyl	[a]	1,3,5 - Triallyl - 2 - allyloxy-4-hydroxybenzene

[a] In these cases the original ether underwent rearrangement during its purification by vacuum distillation. [b] 1-Allyl-2,4-dihydroxybenzene.

BOILING POINTS AND ANALYTICAL DATA*

No.	Boiling point °C.	Mm.	Formula	Analyses, % Calcd.	Found	
1	See Reference 2 for boiling point and analytical data					
2	(Lead salt of 1)		$C_9H_8O_2Pb$	Pb, 58.3	58.6	58.2
3	165–170	25	$C_{12}H_{14}O_2$	C, 75.8	75.76	76.15
				H, 7.57	7.43	7.57
4	(Lead salt of 3)		$C_{12}H_{12}O_2Pb$	Pb, 52.8	50.7	52.5
5	162–165	20	....	...	...	...
6	186–189	22	....	...	...	...
7	(Lead salt of 6)		$C_{15}H_{16}O_2Pb$	Pb, 47.6	48.3	48.1
8	196–200	22	....	...	...	...
9	(Lead salt of 8)		$C_{18}H_{20}O_2Pb$	Pb, 43.6	43.0	43.9
10	144–146	5	$C_9H_{10}O_2$	C, 72.0	71.5	
				H, 6.67	6.97	
11	160–163	5	$C_{12}H_{14}O_2$	C, 75.8	75.3	
				H, 7.37	7.16	
12	182–184	5	....	Analyzed as phenyl isocyanate derivative (below)		

Pyrolysis of the Monoallyl Ether of Resorcinol.—Twenty-two g. of the purified ether was placed in a flask which was heated in a salt-bath. The nature of the exothermic reaction was followed by observing the inner temperature of the flask and the outer temperature of the bath at one-minute intervals.

	Start	1 min.	2	3	4	5	6	7
Inner temp., °C.	170	180	212	280	265	260	248	246
Outer temp., °C.	200	220	226	240	245	245	245	246

The yield of 4-allylresorcinol, which boiled at 144–146° and 5 mm., was 10 g. or 45% of the theoretical.

In another experiment 40 g. of the ether was taken. At an outer temperature of 235°, the inner temperature ascended to 310° and the contents of the flask were boiling vigorously. Only 5 g. of distillate could be obtained from this. It was a very viscous, red liquid which hardened on standing. The residue in the flask solidified to an amber resin. It fused at 95–100°. This material dissolved readily in ether, acetone and 10% sodium hydroxide solution. The alkaline solution was dark red. It was also soluble in hot toluene, hot benzene and hot alcohol. When these solutions were cooled, only tarry material separated. Water, ligroin or carbon disulfide failed to dissolve it.

Quantities less than 20–25 g. should be taken to avoid this vigorous exothermic reaction which leads to tars. In addition to this precaution the heat should be removed from underneath the bath once the exothermic reaction starts.

Proof of Structure of 4-Allylresorcinol

4-Propenylresorcinol.—Four g. of the allylresorcinol, formed by pyrolyzing resorcinol monoallyl ether, was heated[8] at 180° with 5 g. of potassium hydroxide. The product was then dissolved in water and acidified. The oil was separated. It was not purified[9] but was methylated directly.

The methylation into 1-propenyl-2,4-dimethoxybenzene was conducted in the usual way with an excess of dimethyl sulfate and 30% sodium hydroxide solution. The product was oxidized directly by potassium permanganate solution which was slightly alkaline. After filtering off the manganese dioxide and subsequent concentration of the filtrate, the latter was acidified. The cloudy solution was extracted with ether. The red oil thus isolated was crystallized from hot water. Animal charcoal was used to decolorize the solution. About 0.5 g. of 2,4-dimethoxybenzoic acid, melting at 106–109°, was thus produced.

1-Allyl-2,4-dimethoxybenzene.—A portion of the 4-allylresorcinol was methylated directly by dimethyl sulfate and alkali. The allyl-2,4-dimethoxybenzene thus produced was a liquid possessing these physical properties: b. p. 82–85' at 4 mm.; ng 1.5318; n_D^{20} 1.5294.

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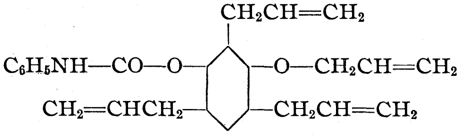
[8] A temperature of 200" was found to give rise to much tarry material.

[9] Using a similar procedure, it was demonstrated that eugenol rearranged into isoeugenol in yields of more than 60%.

Anal. Subs., 0.2664: CO_2, 0.7292; H_2O, 0.1880. Calcd. for $C_{11}H_{14}O_2$: C, 74.1; H, 7.83. Found: C, 74.4; H, 7.85.

1-Propenyl-2,4-dimethoxybenzene and its Oxidation.—As with 4-allylresorcinol, 2 g. of its dimethyl ether was heated for one hour with moistened potassium hydroxide at 160°. The propenyldimethoxybenzene was worked up as in the former case. Oxidation of this material also yielded the 2,4-dimethoxybenzoic acid. With one crystallization it melted for the most part at 104–107°; the final traces melted at 110°.

Structure of 1,3,5-Triallyl-2-allyloxy-4-hydroxybenzene.—To establish the presence of one or two free hydroxyls in the product of rearrangement of the diallyl ether of diallylresorcinol, 1 cc. of the rearranged product (b. p. (5 mm.) 182–184°) was heated with 1 cc. of phenyl isocyanate. The crystals which formed were filtered off and washed with ether. This urethan was readily soluble in hot alcohol, from which it crystallized nicely on cooling; m. p. 160–161°. Analysis revealed the presence of but one nitrogen atom per molecule of substance. Thus the formula is



Anal. (Kjeldahl). Calcd. for $C_{24}H_{27}O_3N$: N, 3.71. Found: 4.19, 3.87.

Summary

The allyl ethers of catechol and of resorcinol rearrange by heating, in a manner which is characteristic of other aryl allyl ethers. Allylcatechols and allylresorcinols are thereby formed. Allyl ethers of these substances, in turn, rearrange similarly in all cases where rearrangement is anticipated. The monoallyl ether of resorcinol gives rise to 4-allylresorcinol rather than the 2-isomer. Both allyl groups in the diallyl ether of diallylcatechol wander from the oxygen to the nucleus, and tetra-allylcatechol is formed. As would be expected, only one of the two groups in the analogous resorcinol compound undergoes a similar rearrangement.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE HYGIENIC LABORATORY, U. S. PUBLIC HEALTH SERVICE]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XXVI. THE RING STRUCTURES OF VARIOUS COMPOUND SUGARS[1]

BY C. S. HUDSON

RECEIVED FEBRUARY 3, 1930 PUBLISHED APRIL 7, 1930

1. Introduction.—During the more recent development of our knowledge of the structures of compound natural sugars, which has come principally from the researches of Haworth, Irvine (concerning maltose and sucrose), Zemplén (concerning cellobiose, lactose, maltose, melezitose and turanose), Helferich (concerning gentiobiose) and Levene (concerning lactose and cellobiose) the writer has sought to use the results as the basis for comparing the rotations of such sugars and their derivatives in order to determine to what extent the rules of isorotation hold among them. In some comparisons the rules held closely but in the case of maltose wide divergence was apparent, a divergence so great as to suggest that the accepted structure of this sugar might be in error. In the case of sucrose, raffinose and gentianose the writer could not reconcile the ease with which the fructose molecule is split off through acid hydrolysis with the 2,5-ring structure that has been assigned to this component by Haworth from methylation studies; a 2,4-ring structure seemed far more probable from the previous assignment[2] of this ring to the easily hydrolyzed glycosides in the mannose and rhamnose series. The writer saw that the isorotation rules were not necessarily in conflict with the specific structural allocations that had come from the researches of Zemplén regarding cellobiose, lactose and maltose, of Helferich regarding gentiobiose, and of Levene regarding cellobiose and lactose, nor with that phase of the methylation researches of Haworth through which he had assigned the 4-glycosidic union to cellobiose, lactose and maltose and the 6-union to melibiose and gentiobiose. On the other hand, the divergencies in the case of maltose, sucrose, raffinose and gentianose could be accounted for by the assumption that a shifting of a ring takes place during the methylation of these sugars. The writer did not publish these various considerations because he was disinclined to dispute the generally accepted assumption of ring stability during methylation in the absence of definite experimental proof of its invalidity. Instead, there was sought some way by which this hypothesis could be tested decisively. This has now been done and the results, which are shown in the preceding article,[3] prove that ring shifting is a frequent occurrence

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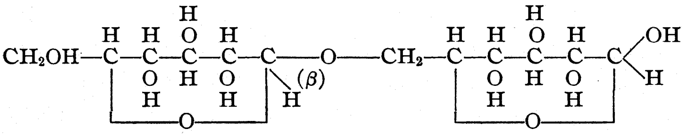
[1] Publication authorized by the Surgeon General of the U. S. Public Health Service. Article XXV was published in THIS JOURNAL, *52*, 1680 (1930).

[2] Hudson, THIS JOURNAL, 48, 1434 (1926).

[3] Hudson, *ibid.*, *52*, 1680 (1930).

during the methylation of glycosides. This disclosure, some of the fruits of which are shown in the preceding article, makes it necessary to reconsider all the structures of the compound sugars, especially the ring assignments, that have become current in recent years. This task will now be undertaken for most of the compound sugars; the results may be stated briefly to be that certain of the results from methylation studies agree with the isorotation rules, indicating ring stability during the methylation of 1,5-ring glycosides and that certain other results from methylation studies can only be reconciled with the rules by the view that a 1,3- or a 1,4-ring glycoside can shift during the methylation of some types of sugars. In the case of maltose, sucrose, raffinose, gentianose and melibiose the rules indicate structures that are different from those now generally accepted.

2. The Structure and Configuration of **Gentiobiose.**—The writer regards the synthesis of this disaccharide by Helferich[4] and his collaborators as conclusively establishing the disaccharide union at Carbon 6 of the primary[5] glucose molecule. The primary ring of the known crystalline gentiobiose must be the same as that in a- and β-methylgentiobioside; this was proved by Hudson and Johnson from rotatory relations.[6] The fact that Helferich synthesized a-methylgentiobioside from normal a-methylglucoside, for which the 1,B = 1,5 ring was proved in the preceding article, shows that the primary ring in the substances cited is 1,B = 1,5. Helferich's use of acetobromoglucose in the synthesis of gentiobiose is very strong evidence that the second glucose component carries a 1,5-ring and is a beta form, because normal β-methylglucoside (1,5) results from this Koenigs–Knorr synthesis when acetobromoglucose unites with methyl alcohol. The β-glycosidic structure of gentiobiose is further supported from the known hydrolysis and also the synthesis of gentiobiose by emulsin.[7] The beta crystalline form of gentiobiose is therefore 6-β-*d*-glucosido-(1,5)-β-*d*-glucose-(1,5) and its configurational formula is (I).



$$\mathrm{CH_2OH{-}\overset{H}{C}{-}\underset{\underset{H}{O}}{\overset{H}{C}}{-}\underset{H}{\overset{\overset{H}{O}}{C}}{-}\underset{\underset{H}{O}}{\overset{H}{C}}{-}\underset{H}{C}{-}O{-}CH_2{-}\overset{H}{C}{-}\underset{\underset{H}{O}}{\overset{H}{C}}{-}\underset{H}{\overset{\overset{H}{O}}{C}}{-}\underset{\underset{H}{O}}{\overset{H}{C}}{-}C{<}^{OH}_{H}}$$

(I) Beta Gentiobiose

The observed initial rotation of β-gentiobiose ($[\alpha]_D$ −11) indicates that the rotation of a-gentiobiose of the same 1,5 primary ring structure may be

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[4] Helferich, Bäuerlein and Wiegand, *Ann.*, 447, 27 (1926).

[5] For brevity the reducing component of a reducing disaccharide will be designated as the primary monosaccharide and its ring as the primary ring; the glycosidic component of the disaccharide will be designated the secondary sugar and its ring the secondary ring.

[6] Hudson and Johnson, THIS JOURNAL, 37,1270 (1915).

[7] Bourquelot, Hérissey and Coirre, *Compt. rend.*, 157,732 (1913).

expected to be about 44. Bourquelot and Hérissey[8,9] have crystallized a form of gentiobiose with 2 moles of methyl alcohol of crystallization, the initial rotation of which is near 18 for the gentiobiose component. The great divergence of this value from the calculation suggests to the writer that either (1) the experimental measurement or purity of the substance may be questionable or (2) that the substance possesses a primary ring other than 1,5. Pollowing the second alternative, let the rotation of α-gentiobiose of the 3,4 primary ring be calculated by the rules of isorotation. The molecular rotation of the known a-d-glucose (1,5) is 20,300, that of the unknown a-d-glucose[2] (1,4) is 11,900 and the difference is 8400 or in the $[\alpha]_D$ value of gentiobiose 8400/342 = 25. If this be subtracted from the calculated rotation of a-gentiobiose of the 1,5-primary ring (44), there is obtained for the a-gentiobiose of the 1,4 primary ring $[a]_D$ 19. The nearness of this value to the rotation observed by Bourquelot and Hérissey (18) is an indication that their substance may possess the 1,4 primary ring. The result is only an indication, however, not a proof, and the question must await further experimental studies before decision can be reached; it is quite possible that a repetition of the preparation may give an initial rotation near 44 rather than 19.

3. The Structure and Configuration of **Trehalose.**—The writer expressed the view fourteen years ago that the high dextrorotations of trehalose and its octa-acetate indicate that this disaccharide is composed of two molecules of *α-d*-glucose.[9] Today our knowledge of ring structures of the 1,4 and 1,5 type in the glucose series permits a more specific study of this question by the same considerations that were used formerly. There are four possible combinations in the trehalose group whose rotations can be calculated. The results are shown in Table I; the data for the calculations

TABLE I

CALCULATED ROTATIONS OF SOME SUGARS OF THE TREHALOSE GROUP

Substance	$[M]_D$ calcd.	$[\alpha]_D$ calcd.
a-d-Glucose (1,4) < > *β-d*-glucose (1,4)	11,880 − 5040 = 6840	20
a-d-Glucose (1,5) < > p-d-glucose (1,5)	20,300 + 3420 = 23,720	69
a-d-Glucose (1,4) < > *β-d*-glucose (1,5)	11,880 + 3420 = 15,300	45
a-d-Glucose (1,5) < > *β-d*-glucose (1,4)	20,300 − 5040 = 15,260	45

are the known rotations of the a- and β-forms of d-glucose (1,5), namely, $[\alpha]_D$ 113 and 19, and the calculated rotations[2] of the similar forms of d-glucose (1,4), namely, 66 and —28, all of which are expressed in the table as molecular rotations (m. w. 180). No one of the calculated rotations is at all near the very high dextrorotation of trehalose (197) and it is evident that the sugar is a combination of two molecules of alpha forms of d-glucose

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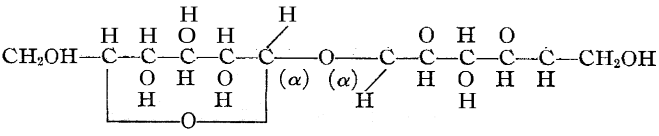
[8] Bourquelot and Hérissey, *J. pharm. chim.*, 16, 418 (1902).

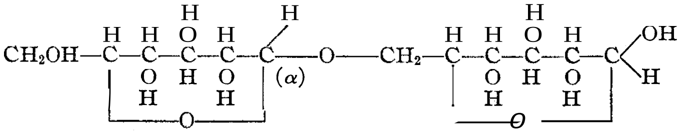
[9] Hudson, THIS JOURNAL, 38, 1566 (1916).

but it may be any one of the three possible combinations $\alpha(1,4) <> \alpha(1,4)$, $\alpha(1,5) <> \alpha(1,5)$ and $\alpha(1,4) <> \alpha(1,5)$. Selection among these possibilities can be made by the following additional consideration. The assignment of each of these structures to trehalose gives the following values for $2A'$ (see the older article)[9] in the designated order: 60,560, 43,680 and 52,100. It will be shown in the subsequent parts of the present article that one of these values (43,680), and only this one, fits in with the rotations of gentiobiose, melibiose, cellobiose and maltose to yield a uniform simple system which correlates the rotations and structures of the compound sugars by the rules of isorotation. The rotation of the octa-acetate of trehalose also fits in with the rotations of the octa-acetates of the four named sugars and one other (paragraph 8) only on the same assumption of structure. These independent results show that the full configuration of trehalose corresponds with (II) and that the sugar is a-d-glucose (1,5)<>a-d-glucose (1,5).



(II) Trehalose

4. Calculation of the Rotation of the Unknown Disaccharide **6-α-*d*-Glucosido-(1,5)-β-*d*-glucose (1,5).**—This sugar, which is now unknown, differs from β-gentiobiose solely in being an alpha glucoside where β-gentiobiose is a beta glucoside. Its configuration is shown in (III).



(III) 6-α-*d*-Glucosido (1,5)-β-*d*-glucose (1,5)

The rotations of the two sugars differ because in β-gentiobiose the value for Carbon 1 of the secondary glucose is to be written $-A^r$ whereas in the unknown sugar it becomes $+A'$; the remaining asymmetric carbons of the two sugars are to be assigned the same summation value B' by the optical superposition rule. We then have for the molecular rotations: β-gentiobiose, $[M]_D = B' - A' = -3800$; 6-α-*d*-glucosido(1,5)-β-*d*-glucose-(1,5), $[M]_D = B' + A' = X$. Let it now be assumed that the value of A' is constant among the compound sugars; it is obtainable[10] from the rotations of trehalose and the known forms of glucose as $A' = 21,840$ and hence $X = +39,880$. The $[\alpha]_D$ value of the beta form of this unknown sugar is

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[10] Ref. 9 and paragraph 3 of the present article.

thus 39,880/342 = +117 and the rotation of its alpha form is 117 + $2a_{OH}$/342 = +166.[11]

5. The Structure and Configuration of **Melibiose.**—The recent methylation studies of Haworth and his collaborators[12] indicate that the 6-union is present in melibiose; the writer accepts this particular methylation datum because any ring shifting during methylation could not affect the result as regards the 6-union. Proof that the primary ring of crystalline β-melibiose (124) is of the 1,5 type is obtained through the writer's observation[9] that the rotation of this disaccharide may be accurately calculated from that of raffinose by the constants that are derivable from the rotations of β-gentiobiose (1,5 primary) and gentianose or of β-glucose (1,5) and sucrose. The presence of an alpha rather than a beta galactosidic residue in melibiose is shown by the failure of emulsin to hydrolyze the sugar; it is also indicated in a rough way by the high dextrorotation of melibiose and in a precise quantitative way by the results of the calculations which will appear in the course of the present discussion. Let us now assume that the secondary ring of melibiose is of the same type as that which exists in alpha methylgalactoside, namely, the 1,4-ring, as shown in the preceding article; the structure of beta melibiose is thus postulated to be 6-α-*d*-galactosido(1,4)-β-*d*-glucose(1,5). The rotation that is to be expected for a sugar of this structure will now be calculated from the rotations of known substances by application of the isorotation rules. The calculation starts with the rotation of beta gentiobiose, the complete structure of which has been established, and proceeds first to the calculation of the rotation of 6-α-*d*-glucosido(1,5)-β-*d*-glucose(1,5), as shown in paragraph 4. The rotation of β-melibiose is then obtainable from that of 6-α-*d*-glucosido(1,5)-β-*d*-glucose(1,5) by adding the value $Ga - G$,[9] obtainable from the molecular rotations of α-methyl-*d*-galactoside(1,4) (37,380) and α-methyl-*d*-glucoside(1,5) (30,630) as 6750 or 20° in the $[\alpha]_D$ value of a di-hexose. The calculated rotation of β-melibiose is thus $[\alpha]_D = 117 + 20 = 137$, which is near the observed value (124). The difference (13) is not large enough to indicate a different ring structure from that assumed, especially in view of the result that will next be shown from a similar calculation of the rotation of the beta octa-acetate of melibiose. Starting with the known β-gentiobiose (1,5 primary) octa-acetate (M = −3590), the addition of $2A'' = 69{,}320$ from trehalose octa-acetate[8] and of 1810 from the difference between the rotations of the tetra-acetates of β-methylgalactoside and β-methylglucoside, gives for β-melibiose((1,5) primary) octa-acetate $[\alpha]_D$ 100, in close agreement with the rotation (102.5) of the

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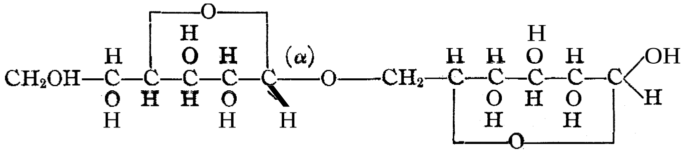
[11] Hudson and Yanovsky, THIS JOURNAL, 39, 1013 (1917); $2a_{OH} = 16{,}900$, from the molecular rotations of alpha and beta glucose.

[12] Haworth, Hirst and Ruell, *J. Chem. Soc.*, 3125 (1923); Charlton, Haworth and Hickinbottom, *ibid.*, 1527 (1927); Haworth, Loach and Long, *ibid.*, 3146 (1927).

known melibiose octa-acetate. The isorotation rules thus indicate that the full structure of β-melibiose is (IV).



(IV) Beta Melibiose

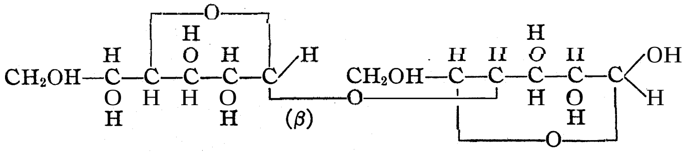
6. The Structures and Configurations of Lactose and Cellobiose.—Accepting the proof of Zemplén that the disaccharide union in these sugars is at Carbon 4 of the primary glucose molecule, it is evident that the sugars cannot possess the 1,4 primary ring and hence the 1,5-ring is assigned to them. Their low dextrorotations and their hydrolysis by emulsin indicate that they are beta glycosides. The secondary rings can be allocated by the following considerations. The various values of the molecular difference between an a-methylgalactoside and glucoside of the 1,4- and 1,5-ring structures are shown in Table II from the data of the preceding article.

TABLE II

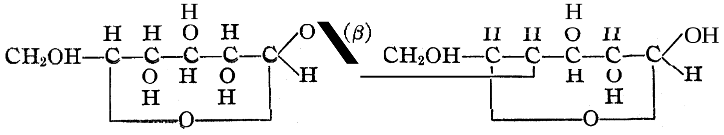
MOLECULAR DIFFERENCE OF ROTATION FOR VARIOUS PAIRS OF METHYL GLYCOSIDES

a-Methylgalactoside (1,4)	**37,380**	**a-Methylgalactoside (1,5)**	**45,930**
a-Methylglucoside (1,5)	**30,830**	**a-Methylglucoside (1,4)**	**22,330**
	6,550		**23,600**
α-Methylgalactoside (1,4)	37,380	α-Methylgalactoside (1,5)	45,930
α-Methylglucoside (1,4)	22,330	α-Methylglucoside (1,5)	30,830
	15,050		15,100

The value of the molecular difference in the case of β-lactose and β-cellobiose[9] is $(35-16)\ 342 = 6498$, and it is seen that this value agrees closely with one of the differences shown in the table but is far removed from the other three. From this good evidence the writer allocates the 1,4 secondary ring to lactose and the 1,5 secondary ring to cellobiose, and the full configurations of the sugars are (V) and VI).

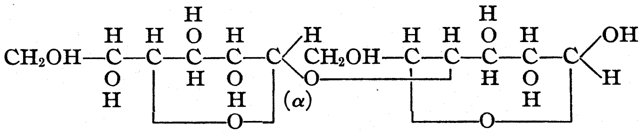


(V) Beta Lactose



(VI) Beta Cellobiose

7. The Structure and Configuration of Maltose.—It was shown in the preceding article that the researches of Pischer and Armstrong in union with the recent work of Zemplén indicates that the primary ring of β-methylmaltoside is 1,5. The results of the writer from rotatory relations[13] show that 8-maltose possesses the same primary ring as β-methylmaltoside. Zemplén has proved that the disaccharide union in maltose is at Carbon 4 of the primary glucose molecule. The high dextrorotation of maltose and the fact that emulsin does not hydrolyze it show that it is an alpha glycoside. Its secondary ring can be allocated by the following considerations. Starting with the molecular rotation of β-cellobiose (5470) and adding the value of $2A' = 43{,}680$ from the rotation of trehalose (see paragraph **3),** the rotation of the hypothetical 4-α-glucosido(1,5)-β-*d*-glucose(1,5) is calculated from the same considerations that were described in paragraph 4 to be $[\alpha]_D = (5470 + 43{,}680)/342 = 144$. This value is so much greater than that observed for 8-maltose (118) that the writer concludes that the 1,5 secondary ring cannot be possessed by maltose. On the other hand, it can be shown that this ring is of the 1,4 type. The difference between the molecular rotations of the a-d-glucoses of the 1,5- and 1,4-ring types, respectively, is $20{,}300 - 11{,}880 = 8420$ from Table I. Subtracting this quantity from the rotation just calculated gives $[\alpha]_D = (5470 + 43{,}680 - 8420)/342 = 119$ as the rotation of 4-α-*d*-glucosido(1,4)-β-*d*-glucose-(15) This rotation agrees so closely with that of β-maltose (118) that the 1,4 secondary ring may be assigned to the sugar and its full configuration becomes (VII).



(VII) Beta Maltose

This novel result is confirmed by the similar consideration of the rotation of β-maltose octa-acetate. Adding $2A''$ (69,320, from trehalose octa-acetate)[9] to the rotation of β-cellobiose octa-acetate (—9900) gives $[\alpha]_D = (-9900 + 69{,}320)/678 = 88$ for the rotation of the beta octa-acetate of 4-α-*d*-glucosido(1,5)-*d*-glucose(1,5); this value is much greater than that observed for β-maltose octa-acetate (62.7). On the other hand, the value calculated for the beta octa-acetate of 4-α-*d*-glucosido(1,4)-*d*-glucose(1,5) is [a], $= (-9900 + 69{,}320 - 18{,}462)/678 = 60$, which agrees closely with the rotation of β-maltose octa-acetate.'' These two independent proofs of the 1,4 secondary ring structure of maltose can be reconciled with

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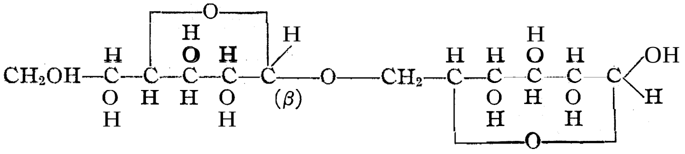
[13] Hudson. THIS JOURNAL, 47, 268 (1925); *Scientific Papers of the U. S. Bureau of Standards,* No. 533, pp. 363–364 (1926).

[14] The value 18,462 is the difference between the molecular rotations of the α-methylglucoside tetra-acetates of the 1,5- and 1.4-rings, respectively (Ref. 2).

the agreeing methylation results of Irvine and of Haworth, who obtained normal tetra-methylglucose(1,5) by the hydrolysis of fully methylated maltose, only on the view that the secondary 1,4-ring shifts to the 1,5-position during methylation. This new structure for maltose opens a wide field for speculation and experimental research. Maltose and cellobiose are not structurally similar sugars, as has been postulated during recent years, and it may consequently be that starch and cellulose differ profoundly in structure. The validity of methylation evidence in studying the structures of both these polysaccharides can no longer be regarded as secure because of the ring shifting that has been shown in the case of the secondary 1,4-ring of maltose. In the field of enzyme studies one sees that a-glucosidase and maltase hydrolyze different ring types of d-glucosides, the former attacking 1,5-ring a-glucosides and the latter an α-glucoside of the 1,4-ring.

8. The Structure and Configuration of the Synthetic Disaccharide, **6-β-*d*-Galactosido-*d*-glucose,** of Helferich and **Rauch.**—These workers[15] have synthesized the octa-acetate of a new disaccharide for which they have proved the structure 6-β-*d*-galactosido-β-*d*-glucose octa-acetate, leaving only the two rings to be allocated. The primary ring is 1,5 because Helferich's synthesis of β-gentiobiose octa-acetate by like reactions in which acetobromoglucose was used in place of acetobromogalactose proves that the tetra-acetylglucose common to both syntheses possesses a 1,5-ring and is a beta form. Acetobromogalactose yields with methyl alcohol in the Koenigs–Knorr synthesis the beta methylgalactoside to which the 1,4-ring was assigned in the preceding article and the writer assumes that the galactose component of the new disaccharide therefore possesses the same 1,4-ring. It thus results that we have in the beta octa-acetates of melibiose and the new sugar a pair of known substances from which a value of $2A''$ can be obtained and it can be determined whether it agrees with the value obtained from trehalose octa-acetate ($2A'' = 69{,}320$); the molecular rotation of beta melibiose octa-acetate is 69,500 and that reported by Helferich and Rauch for the beta octa-acetate of their new disaccharide is zero, hence $2A'' = 69{,}500$ for this pair. The agreement is excellent and the full structure and configuration of the new sugar in the form present in its beta octa-acetate is thus shown to be (VIII).



(VIII) 6-β-*d*-Galactosido (1,4)-β-*d*-glucose (1,5)

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[15] Helferich and Rauch, *Ber.*, 59, 2655 (1926). Dr. Helferich informs the writer that the solvent in which the rotation of the octa-acetate was measured and found to be zero was chloroform, which is not stated in the original article, and that a recent repetition of the measurement has given the same result.

9. Proof of the Invalidity of **Haworth's**[16] **Application** of the Isorotation Rules to Maltose and **Cellobiose.**—Haworth obtains from beta cellobiose and beta maltose, through the assignment of a 1,5-secondary ring to maltose, the value $2A' = (118 - 16)342 = 34{,}884$, and for the beta octa-acetates of these sugars the value $2A'' = 52{,}400$. It readily can be shown that these values are so low that they must be rejected as impossible ones, and the evidence is precisely that which Haworth has advanced in proof of their correctness. He shows that the value of 2A from the alpha and beta methylglucosides or galactosides is about 37,460, and that the similar value for the tetra-acetates of these substances is about 53,500 and claims that the approximate agreement thus shown with the values from the maltose–cellobiose series proves that his ring assignments are correct. The error in the argument lies in his overlooking the well-established fact[17] that the rotation of Carbon 1 in a methyl glycoside is much lower than for glycosides with heavier groups than methyl attached; the value for $2A'$ in the disaccharide must be far larger than the $2A$ of the methylglycosides. Some recent evidence on this subject has been obtained by Pacsu[18] through the preparation of the alpha and beta forms of cyclohexanol-glucoside and their tetra-acetates. The value of $2A'$ for these glycosides is found to be 45,750 and that of $2A''$ for their acetates to be 62,560. These values are far greater than those from the methyl glycosides and their acetates and the values used by Haworth but are comparable with the higher values that the writer has accepted for the compound sugars. The explanation of the low values of Haworth is that the secondary ring of maltose is not 1,5 but rather 1,4, as shown in paragraph 7; on the methylation of maltose this ring shifts to the 1,5-position.

10. The Structure and Configuration of Sucrose.—The writer showed some years ago[19] that the hydrolysis of sucrose by invertase yields as the first detectable hexoses the form of a-d-glucose (113) to which the 1,5-ring is now assigned and a form of fructose, of $[\alpha]_D +17$, which he then designated as a-fructose because of its mutarotation in the levo direction. It is a remarkable experimental fact, to which too little attention has been paid in recent years, that the nearly instantaneous hydrolysis of sucrose by very strong invertase preparations yields initially a mixture of hexoses having a mean rotation of the same value as that of sucrose. For many years this accurate observation could not be reconciled by the writer with structural considerations because if sucrose is composed of alpha forms of both glucose and fructose, its rapid enzymotic hydrolysis should result in a large initial drop in dextrorotation. Consider for example the case of the enzymotic

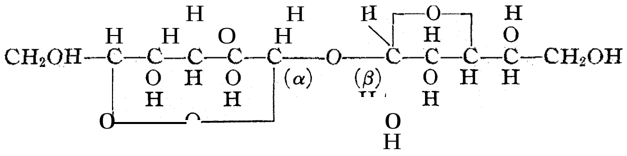
[16] Ref. 12, second article.

[17] Hudson, THIS JOURNAL, 31, **82** (1909).

[18] The article by Eugen Pacsu on this subject is now in press and will appear shortly; the writer is indebted to him for kind permission to use his results.

[19] Hudson, THIS JOURNAL, 31,655 (1909).

hydrolysis of trehalose, of the structure α-glucose(1,5) $<>$ α-glucose(1,5), which is assumed to be so rapid that the sugar is completely hydrolyzed before the mutarotation of the resulting α-glucose(1,5) reaches sensible proportions. The $[\alpha]_D$ value of the solution should drop on hydrolysis immediately from 197, the rotation of trehalose, to about 113, the rotation of α-glucose(1,5). In the case of the unknown β,β-trehalose, of the structure β-glucose(1,5) $<>$ β-glucose(1,5), the rotation of which has been calculated[g] to be $[\alpha]_D$ -58, a similar enzymotic hydrolysis should cause the rotation to rise immediately from -58 to about $+19$, the rotation of β-glucose(1,5). However, in the case of the hydrolysis of the unknown a,-,!?-trehalose (calculated $[\alpha]_D$ 70) the rotation should not change immediately because it is the average of the rotations of its constituent alpha and beta glucoses. It would thus seem that the form of fructose which is initially liberated from sucrose (and from raffinose and gentianose, which are derivatives of sucrose by the attachment of another hexose molecule to the glucose constituent of sucrose) is a beta form of the observed $[\alpha]_D$ $+17$. The alpha form of this type of fructose would necessarily be a very strongly dextrorotatory substance of $[\alpha]_D$ approximately $+111$ if the difference ($2a_{OH}$) in the fructose series is the same as for the forms of glucose. If these considerations are correct, however, how can the fact be explained that this initially liberated fructose, of $[\alpha]_D$ 17, acts like an alpha sugar by mutarotating to the strongly negative rotation (-90) of stable fructose solutions? The fructose actually behaves like an a-form, judging from its mutarotation, but like a β-form, judging from the absence of an immediate change following the nearly instantaneous hydrolysis of sucrose. The writer made these observations in 1909; it is now apparent through the knowledge that has been gained in the subsequent years concerning the occurrence of various ring types among the sugars that the measurements furnish clear proof that the initially liberated fructose is indeed a beta-form but that it shifts its ring during the mutarotation. With this point cleared up one may proceed with the study of the structure of sucrose by rotatory considerations. We start then with the view that sucrose is α-*d*-glucose(1,5) $<>$ β-fructose(2,?), from the evidence that has been discussed, and the sole problem remaining is to allocate the position of the fructose ring. It cannot be 2,5 because the rotation of α-*d*-glucose(1,5) $<>$ β-*d*-fructose(2,5) may be calculated from those of the known α-methyl-*d*-glucoside(1,5) (30,830) and β-methyl-*d*-fructoside(2,5) ($-33{,}400$) to be $[\alpha]_D = (30{,}830 - 33{,}400)/342 = -8$, which is far different from the rotation of sucrose (66). Haworth has assigned this 2,5-ring structure to the fructose portion of sucrose from his methylation evidence; it is clear that this ring cannot be present and assuming the correctness of his experimental identifications of the methylated products one can only conclude that the fructose ring has shifted during methylation. Let the possibility that the fructose ring may be 2,6 be examined; referring to the preceding article, paragraph 20, it is evident that β-methyl-*d*-fructoside(2,6) must be a more strongly levorotatory substance than β-methyl-*d*-fructoside(2,5) in analogy with the corresponding substances of the d-arabinose series and that consequently α-*d*-glucose(1,5)< >β-*d*-fructose(2,6) will have a greater levorotation than the value $[\alpha]_D$ −8, mentioned previously. This result excludes the possibility of the 2,6-ring, and unless one assumes an ethylene oxide ring, which appears highly improbable because of instability, the assignment of the 2,4-ring becomes necessary and sucrose is α-*d*-glucose-(1,5)< >β-*d*-fructose(2,4) as shown in the full configurational formula (IX).



(IX) Sucrose

The rotation of the octa-acetate of sucrose ($[\alpha]_D$ 59.6) supports the foregoing results. The rotation of the octa-acetate of α-*d*-glucose(1,5)< >β-*d*-fructose(2,5) is calculated from the rotations of the tetra-acetates of α-methyl-*d*-glucoside(1,5) ($[M]_D$ 47,300) and β-methyl-*d*-fructoside(2,5) (−45,100) to be $[\alpha]_D = (47{,}300 - 45{,}100)/678 = 3°$, which is greatly different from the value for sucrose octa-acetate. The assignment of the 2,6-ring leads to a value even more divergent and one is thus led to assign the 2,4-ring. The ease with which sucrose is hydrolyzed by acids conforms with the assigned configuration; the propylene oxide ring of its fructose component is the 1,C = 1,3[2] ring of the mannose, rhamnose and lyxose series and sucrose properly takes its place beside the very easily hydrolyzed methylmannoside, methylrhamnoside and methyllyxoside of this ring type, as was suggested in paragraph one.[20]

11. The Structures and Configurations of Raffinose and Gentianose.—The configurations that have been shown for melibiose, gentiobiose and sucrose enable one to write the following full configurations for these trisaccharides (X and XI).

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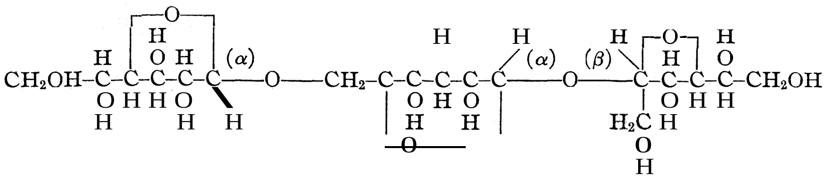
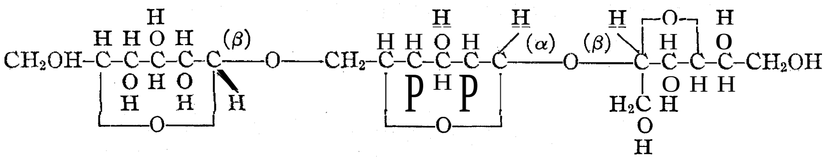
[20] In a recent article Haworth, Hirst and Miller [*J. Chem. Soc.*, 2469 (1929)] attempt to support their assumption of a 1,5-ring in these easily hydrolyzed glycosides by suggesting a new type of stereoisomerism which is in conflict with the Le Bel–van't Hoff theory of the asymmetric carbon atom as heretofore applied in the sugar group; since their experimental results are readily intelligible on the view that the 1,3-ring can shift during methylation and since such shiftings of 1,3- and 1,4-rings have been demonstrated in numerous cases in this article and the preceding one, their discussion of the supposed invalidity of the Le Bel–van't Hoff theory seems to the writer to have no substantial basis.



(X) Raffinose



(XI) Gentianose

Postscript of March 4, 1930.—It will be shown in a later article that the rotations of primverose and its beta hepta-acetate agree with the structure 6-[*β-d*-xylosido(1,5)]-*d*-glucose(1,5), that the structure of vicianose is in all probability 6-[*α-l*-arabinosido(1,5)]-*d*-glucose(1,5) and that vicianin is 6-[*α-l*-arabinosido(1,5)]-*β-d*-glucosido(1,5)-1-mandelonitrile.

12. Summary

The occurrence of ring shifting during the methylation of some glycosides, as was shown in the preceding article, makes it necessary to determine the structures and configurations of the compound sugars by methods which avoid this disturbing complication. It is shown that the isorotation rules apply closely to the group of compound sugars and that the full structures and configurations of these substances can be determined by the use of these rules in conjunction with other data on structure that are valid whether or not ring shifts occur during methylation. The results give new structures for maltose, melibiose, sucrose, gentianose and raffinose.

WASHINGTON D.C.

NOTES

A Note on the Preparation of Lecithin.—The preparation of pure lecithin was recently undertaken in order to study the relation of the pure product to the process of blood coagulation.[1]

The method used was that described by Levene and Rolf;[2] a simplification of similar methods previously used by Bergell,[3] McLean[4] and by Levene[5] and his co-workers. It consists in the simple extraction of dried

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[1] A. Wadsworth, F. Maltaner and E. Maltaner, *Am. J. Physiol.*, *91*, 423 (1930).

[2] P. A. Levene and I. P. Rolf, *J. Biol. Chem.*, *72*, 587 (1927).

[3] P. Bergell, *Ber.*, **33**, 2584 (1900).

[4] H. McLean, *Biochem. J.*, 9, 351 (1915).

[5] P. A. Levene and C. J. West, *J. Biol. Chem.*, *34*, 175 (1918); P. A. Levene and I. P. Rolf, *ibid.*, 46, 353 (1921).

tissue with ethyl alcohol, the chilling out of fats at 0°, precipitation of the lecithin as the cadmium salt, purification of the cadmium salt by exhaustive extraction with ether and recovery of the lecithin by treatment of a chloroform solution of the cadmium salt with a saturated methyl alcohol solution of *dry* ammonia gas, the recovered lecithin being purified further by emulsifying an ether solution in 10% acetic acid and reprecipitating with acetone.

Considerable difficulty was encountered in the precipitation of the cadmium salt. This was found to be due to the use of absolute methyl alcohol in the preparation of the cadmium chloride solution used for precipitation.

It was found after a considerable loss of time and material that a good yield of a satisfactory cadmium lecithin compound could only be obtained by the use of moist (95%), instead of absolute, methyl alcohol for this step of the procedure.

It was further observed that a pure product could be obtained without recourse to the final purification with acetic acid. This acetic acid treatment decreases the yield greatly and tends to darken the product.

It was possible, moreover, to recover a considerable quantity of pure lecithin from the fats originally precipitated at 0° from the alcoholic extracts of tissue by extraction with alcohol at 0° and subsequent precipitation with the 95% methyl alcohol solution of cadmium chloride.

The results obtained in the preparation of lecithin from beef liver and beef heart are tabulated below.

TABLE I

ANALYSIS OF LECITHIN

Lecithin	Carbon, %	Hydrogen, %	Nitrogen, %	Amino Nitrogen, %	Phosphorus, %
Liver lecithin (one acetic acid treatment)	65.18	10.38	1.94	0.005	3.90
Liver lecithin (no acetic acid used)	65.50	10.69	1.82	0.004	3.84
Liver lecithin (recovered from acetone washings)	6462	10.51	1.72	...	3.84
Heart lecithin (no acetic acid used)	64.66	11.14	2.06	0.000	3.87
Oleic-stearic lecithin (calcd.)	65.55	11.01	1.73	0.000	3.85
Oleic–palmitic lecithin (calcd.)	64.81	10.81	1.80	0.000	3.99

CONTRIBUTION FROM THE
DIVISION OF LABORATORIES AND RESEARCH
NEW YORK STATE DEPARTMENT OF HEALTH
ALBANY, NEW YORK

FRANK MALTANER

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PUBLISHED APRIL 7, 1930

Isolation of an Arsenic Compound of Pyridine and Some Observations Concerning the Phase System Arsenic Trichloride–Pyridine.—During the past twenty years many articles have appeared describing reactions that take place between pyridine and inorganic salts. Most of the studies that have been made in this country trace back, directly or indirectly, to Dr. L. Kahlenberg. The studies have usually been accompanied by phase rule interpretations.

In so far as the author knows, no study has been made of the system arsenic trichloride–pyridine, though evidence of reaction between these compounds is recorded in the well-known studies of P. Walden.[1] Walden predicted from conductivity studies that a compound containing one molecule of pyridine and one molecule of arsenic trichloride was formed from interaction between these chemicals, but he made no attempts to isolate or describe any of the properties of such a compound. While a compound of the formula predicted by Walden was not isolated in this work, a compound giving the theoretical arsenic content for the compound $AsCl_3 \cdot 2C_5H_5N$ was isolated.

Experimental.—The best grade of pyridine produced by Kahlbaum was distilled from potassium permanganate, then from fused barium oxide and the fraction coming over between 114.9 and 115.3° at 750 mm. was stored over recently fused potassium hydroxide. Arsenic trichloride of c. p. grade was distilled from recently sublimed metallic arsenic. Upon taking an excess of the purified pyridine (*i. e.*, about 75 mole per cent.), and thoroughly mixing it in a dry container with the prepared arsenic trichloride, there was much heat evolved. Upon cooling in a dry atmosphere distinct rosets of crystals were produced. These crystals were freed from mother liquor by thorough centrifuging. Since the crystals were highly hygroscopic, it was impractical to wash them free of mother liquor by use of organic solvents. The compound was analyzed for arsenic by decomposing it with alkali and titrating with iodine solution. The iodine solution had been carefully standardized against arsenious acid made up from purified and resublimed arsenious oxide. The following analyses were obtained: Sample I, As, 22.11%; II, 21.91%; III, 22.16%. The theoretical amount of arsenic in the compound $AsCl_3 \cdot 2C_5H_5N$ is 22.08%.

Phase rule applications to this system are particularly difficult due to undercooling and to tendency toward obtaining abnormal time–temperature cooling curves. While an arsenic trichloride–pyridine mixture of 66.67 mole per cent., with reference to pyridine, gives a distinct freezing point rise, roughly fixing the melting point for the compound $AsCl_3 \cdot 2C_5H_5N$ at 64°, the curve may or may not be continuous in its rise.

CONTRIBUTION FROM THE
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[1] P. Walden, *Z. physik.* Chem., 43, 446 (1903).

The Preparation of Acetylchloro-aminobenzene.—The physical and chemical properties and the rate and mechanism of the rearrangement of acetylchloro-aminobenzene have been investigated recently in several laboratories.[1] Since the presence of impurities such as acetanilide affect the rearrangement in aqueous solution[1c,2] and in glacial acetic acid,[1c,2] it is desirable to have a method of preparation which will produce acetylchloro-aminobenzene without contamination with other anilides. A method is outlined below which can be relied upon to give a 70% yield of pure acetylchloro-aminobenzene melting at 91° and requiring no further purification.

(A) To a solution of 15 g. of acetanilide (0.11 mole) in 3 liters of water, 16.8 g. of sodium bicarbonate (0.2 mole) is added and the whole is filtered to remove suspended particles.

(B) To 150 cc. of 1.0 M sodium carbonate chlorine gas is added until the solution contains between 1.6×10^{-3} and 1.8×10^{-3} equivalents of chlorine per cc. as determined by analysis of a portion. This is prepared at 5° and the solution is filtered before using.

Solution A is kept at approximately 5° and is stirred slowly by a mechanical device during the dropwise addition of a calculated volume of Solution B. (Too rapid stirring of A may cause precipitation of acetanilide.) The product, acetylchloro-aminobenzene, precipitates toward the end of the addition of the chlorine solution. After standing for about fifteen minutes to insure complete precipitation, the needle-like crystals are removed by filtration, washed with cold water until no further test for chloride ion is obtained and dried at room temperature in a vacuum desiccator over sulfuric acid; yield, 13 g., melting point 90.5–91°.[3]

The product may be recrystallized from a solvent composed of 1 part of acetone and 9 parts of petroleum ether, yielding plate-like crystals which have the same melting point as the needles.

Armstrong[4] prepared the substance at elevated temperatures (50–85°) and obtained fine needles. Chattaway and Orton[6] replied to his statement as to the crystal form as follows: "Acetylchloro-aminobenzene, from whatever solvent it separates, crystallizes, according to our observations in plates or short, four-sided prisms. When needles are present, they are undoubtedly the isomeric *p*-chloro-acetanilide. . . . ." The discovery that the compound may be prepared in either form settles a dispute of long standing.

The method here presented differs from others in use up to the present time in that a sodium bicarbonate buffer is present in the acetanilide solution, which prevents the formation of *o*- and *p*-chloro-acetanilide even

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[1] (a) Mathews and Williamson, THIS JOURNAL, 45,2574 (1923); (b) Orton, Soper and Williams, *J. Chem. Soc.*, 998 (1928); (c) Soper, *J. Phys. Chem.*, *31*, 1193 (1927); (d) Bradfield, *J. Chem. Soc.*, 351 (1928); (e) Porter and Wilbur, THIS JOURNAL, 49, 2145 (1927).

[2] Porter and Barnes, paper ready for publication.

[3] Since the compound decomposes on heating, samples should be placed in the bath, which is already at 82–83°. Then with the usual rate of heating, the product, if pure, will melt at 90.5–91°.

[4] Armstrong, *J. Chem. Soc.*, 77,1047 (1900).

[5] Chattaway and Orton, ibid., 79,274 (1901).

though a chlorine solution is used which is three times the maximum concentration considered safe by Chattaway and Orton.[6] The method is rapid and the product is better than 99.7% pure.

Contribution from the
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C. W. Porter

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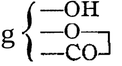
Note on Caryophyllin and Urson.—In a previous article[1] the writer reported the results of an examination of caryophyllin and urson, two very similar and probably isomeric compounds, having apparently the composition $C_{30}H_{48}O_3$ and exhibiting properties which could best be explained by the assumption of an oxy-lactone structure, or the grouping  $\left\{\begin{array}{l}\text{—OH}\\ \text{—O—}\\ \text{—CO—}\end{array}\right.$

More recently urson has been studied by van der Haar,[2] who has arrived at the conclusion that the alternative formula,  $\left\{\begin{array}{l}\text{—OH}\\ \text{—COOH}\end{array}\right.$, which is that of an hydroxy acid, has been demonstrated. The arguments against this formula have already been noted by the writer. Van der Haar also criticizes the methods employed by the writer as "uncontrolirbar" in comparison with elementary analyses, but in reality, the titrations used to show the functional relations of these compounds can be "controlled" or checked with the utmost ease, and they were employed exactly because they are more conclusive and satisfactory for the purpose in view than combustions.

It was found that caryophyllin and urson could be titrated with accuracy in alcoholic solution, the results indicating one carboxyl or lactone group in the C_{30} molecule. On acetylation, two acetates were obtained; one, an unstable diacetate, convertible by boiling with alcohol into a stable monoacetate, which in turn yielded the original caryophyllin or urson by hydrolysis with alkali. These results appeared to be explainable only by the oxy-lactone formula. Van der Haar, however, obtained from urson an acetate, melting at 200°, which on boiling with alcohol gave a compound melting at 275°, which without further examination he assumed to be urson. Inasmuch as urson melts at about 285° and the mono-acetate at about 265°, the identification is rather unsatisfactory. In view of the importance of this fact for his hypothesis, a more thorough examination of the product would have been desirable. A quantitative hydrolysis would have been conclusive. In two later articles[3] van der Haar has revised his previous

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[6] Chattaway and Orton, J. Chem. *Soc.*, **75**, 1046 (1899).

[1] Dodge, This Journal, 40, 1917 (1918).

[2] Van der Haar, *Rec. trav. chim.*, 43, 367, 542 (1924).

[3] Van der Haar, *ibid.*, 46, 775 (1927); 47, 585 (1928).

conclusions and, employing the methods used by the writer finds, in fact, that caryophyllin (which is shown to be identical with the sapogenin of beets, and also with the oleanol of Power and Tutin)[4] yields two acetates. Urson also gave two similar derivatives.

To reconcile these facts with the hydroxy acid formula, which permits but one acetyl derivative, he suggests for the compound described by the writer as diacetate, the formula $[C_{30}H_{48}(OAc)CO]_2OAc_2O$, which represents the anhydride of the acetylated hydroxy acid combined with one molecule of acetic anhydride "of crystallization!" On treatment with alcohol this is supposed to yield the monoacetate, $C_{30}H_{48}(OAc)COOH$.

It is hardly necessary to point out the anomalous nature of this hypothesis. If the first compound is really a molecular compound of an acid anhydride with acetic anhydride, boiling with alcohol should, by all analogy, yield an ester, and not the free acid. To the writer, the lactone formula appears less involved in difficulties.

Van der Haar also claims to have "proved," from the results of two combustions, the formula of urson to be $C_{31}H_{50}O_3$, instead of the previously accepted $C_{30}H_{48}O_3$. How much importance should be ascribed to this is not clear. Equally good analyses may be cited for the latter formula. It is to be noted, however, that Power and Tutin found the composition $C_{31}H_{50}O_3$ for oleanol (probably identical with caryophyllin) and prunol (apparently identical with urson), thus agreeing with van der Haar. The former also described two acetates of oleanol, and considered it to be a phenol. Yet this assumption, as well as the hydroxy acid hypothesis, seems to be contradicted by the insolubility of these compounds in aqueous alkali. Furthermore, both compounds show an unusual stability at high temperatures. They may be sublimed without decomposition: caryophyllin, in fact, is slowly volatile in steam, and has been frequently observed by the writer as an almost pure sublimate on the covers of stills used for the extraction of oil of cloves. This stability seems to the writer to indicate very definitely the lactone structure. Compare, for example, *o*-coumaric acid, a typical hydroxy acid, which decomposes at its melting point, and its lactone, coumarin, which distils without decomposition at 280°.

To sum up, the question as to the elementary composition of these compounds may be considered as open, with the evidence rather in favor of the C_{30} formula. As to the functions of the oxygen atoms, the writer is still of the belief that the lactone formula is the only one available.

CONTRIBUTION FROM THE
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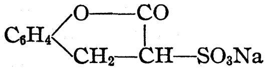
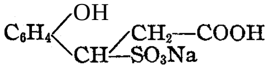
[4] Power and Tutin, **J.** *Chem. Soc.*, **93,891 (1908).**

Some Derivatives of **Coumarin.** 11.—The reaction of coumarin with acid sulfite solutions was found by the writer[1] to result in the formation of sulfonic derivatives of hydrocoumarin, the sodium salt, for example, having the composition $NaSO_3C_9H_7O_2{\cdot}H_2O$, and probably the structure



More recently, Dey and Row[2], by treating coumarin with sodium sulfite and subsequent acidification, obtained a salt $NaSO_3C_9H_9O_3{\cdot}H_2O$, to which they assigned the structure



Inasmuch as the writer had not previously observed the occurrence of an acid salt of this type, and Dey and Row make no reference to the lactone salt already described, it seemed desirable to repeat some of this work in order to characterize more exactly the salt or salts in question. The result of the examination has confirmed the previous work of the writer, and also, to a certain extent, that of Dey and Row.

The lactone salt is obtained by treating coumarin with a solution of sodium acid sulfite. It crystallizes in flat prisms with rectangular ends, under the microscope apparently orthorhombic. The crystals effloresce at the ordinary temperature, and are soluble in about five parts of water at 20°. The fresh solution is neutral to litmus and gives no color with ferric chloride. Addition of salt to the solution precipitates the lactone salt almost completely.

The acid salt is readily prepared as follows: coumarin (20 g.) is dissolved, by moderate heating, in about 100 g. of sodium sulfite solution (25% $Na_2SO_3{\cdot}7H_2O$). If the solution becomes alkaline to phenolphthalein, it may be neutralized with acid sulfite. When all the coumarin is dissolved, the solution is filtered, diluted to about 160 g., 35 cc. of about 4 N hydrochloric acid added and the mixture allowed to crystallize in the cold, or, if large crystals are desired, by slow evaporation at the ordinary temperature.

The acid salt is deposited in large transparent prisms with pyramidal terminations, or, more rarely, in rhombic prisms with basal planes. Sections perpendicular to the prism faces show in convergent polarized light the characteristic interference figure of orthorhombic crystals. The crystals contain $3H_2O$, do not effloresce and are soluble in about three parts of water at 20°. The solution is strongly acid and is not precipitated by the addition of salt.

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[1] Dodge, THIS JOURNAL, 38, 446 (1916).

[2] Dey and Row, J. *Chem. Soc.*, 125,554 (1924).

Anal. 2.00 g. at 105–110° lost 16.63%, 2.001 g. lost 16.55% of water. Calcd. for $3H_2O$: 16.77%. *Titration.* Subs., 1.998, 1.667, 1.4365: 12.4, 10.8, 9.0 cc. of 0.5 N KON. Calcd. acid value: 170.8. Found: 173, 181, 175. Subs., 1.998: Na_2SO_4, 21.4%. Calcd.: 22%.

The slightly high acid values are probably due to the phenolic hydroxyl, as similar high values are obtained in titrating coumaric acid.

The writer was unable to obtain the monohydrated salt described by Dey and Row. In several batches, however, the large prisms were accompanied by groups of silky needles, which could not be readily purified; these also often appear in recrystallizing the pure trihydrate.

With ferric chloride solution the acid salt gives a very characteristic bright blue coloration. A fresh solution of the lactone salt shows, as already stated, no color with this reagent. If, however, the solution is allowed to stand, after a few hours a greenish-blue color is obtained, and after twenty-four hours, a bright blue, indistinguishable from that of the acid salt. This indicates that the lactone salt, in solution, is gradually hydrolyzed to the acid salt, which is exactly what would be expected. For the hydrocoumarin ring, being a saturated δ-lactone, has no longer the characteristic stability of the coumarin ring, but in solution tends to an equilibrium between lactone and acid.

Excess of mineral acid throws the equilibrium point toward the lactone stage, which explains the fact that from the mother liquor of the trihydrate acid salt, some lactone salt can be obtained by salting out.

Very strong acid causes a partial hydrolysis to coumarin. For example, 10 g. of concentrated hydrochloric acid was added to a solution of 6 g. of acid salt in 10 g. of warm water and the mixture evaporated to dryness. On dissolving the residue in 30 cc. of water, 0.8 g. of coumarin remained; the filtrate on addition of salt gave an abundant precipitate of lactone salt.

On heating above 120°, the acid salt, like the lactone salt, yields coumarin.

Summary.—From coumarin, by addition of sodium bisulfite, two distinct salts are obtained: one, a lactone corresponding to hydrocoumarin, the other an acid salt corresponding to hydrocoumaric acid.

CONTRIBUTION FROM THE
LABORATORY OF THE
DODGE AND OLCOTT CO.
BAYONNE, NEW JERSEY

FRANCIS D. DODGE

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NEW BOOKS

A Chemical Dictionary, Containing the Words Generally Used in Chemistry, and Many of the Terms Used in the Related Sciences of Physics, Astrophysics, Mineralogy, Pharmacy, and Biology with Their Pronunciations. Based on Recent Chemical Literature. By INGO W. D. HACKH, Professor of Chemistry, College of Physicians and Surgeons, School of Dentistry, San Francisco, California. P. Blakiston's Son and Co., Inc., Philadelphia, Pennsylvania, 1929. vi + 790 pp. 18 X *25.5* cm. Price $10.00.

This volume, comprising some 30,000 terms, is a serious attempt to provide a moderately comprehensive pronouncing dictionary of chemical terms, and is the first such available in English for more than a century. It is obviously intended to be definitive rather than encyclopedic. The style is uninvolved, the selection of terms on the whole good and the printing and proof reading are satisfactory. The book is embellished with many small halftone portraits of famous chemists in connection with brief biographical data, with some pictures of apparatus and with tables in considerable variety, many of which furnish novel and highly useful arrangements of data.

It is not to be expected that so great a mass of unrelated facts could be assembled without the presence of errors, both of fact and of judgment. A number of rather common terms are not to be found, including ethyl gas, slip, sorbite as a constituent of steel, a-cellulose, doctor solution, hard and soft coal, and Sorel cement. Other terms are incompletely defined with respect to their chemistry; for example, no reference is made to the modern meaning of lacquer, fat and lean as limiting adjectives in the description of ore and clay, the chemical nature of chromel, the compositions of many minerals, and the chemical properties of some elements. The less common dyes, rocks, explosives, theories, laws, and named tests, are for the great part omitted. Pronunciations as a rule are simply and accurately indicated; but there is an obvious error in that of Miiller which is given as *mool-er*. Among the five or six actual errors in fact casually noted, that of pyrex being defined as a trade name for "carbon tetrachloride, used as a fire extinguisher," was the most obvious, for "pyrene" is not defined with this meaning. An occasional tendency toward looseness of grammatical structure has permitted some adjectives (such as hygroscopic and quinquevalent) to be defined as nouns.

A number of terms only distantly related to chemistry are included; fath. (abbreviation of fathom), cardiograph, hibiscus, reductio ad absurdum, Ericinae are examples. Frequently only the commoner and best known forms of apparatus are defined and illustrated by cuts, whereas it is usually the less common forms that most need definition and illustration.

It is unnecessary to emphasize that these matters are of no great importance in comparison with the value of the book as a whole. Both the author and the publishers deserve the thanks of all chemists, the former for the vast amount of time and effort he has given to the compilation, and the latter for their understanding of the need that existed for such a volume in the face of general pessimism on the part of most publishers. In spite of its faults it is vastly superior to any other chemical dictionary in English and becomes at once a necessary part of the working library of every active chemist.

WILLIS A. BOUGHTON

A Text-book of Inorganic Chemistry. Edited by J. NEWTON FRIEND. Vol. VI, Part III. Vanadium, Niobium and Tantalum. By SYDNEY MARKS, M.Sc., A.I.C. J. B. Lippincott Company, Philadelphia, Pa., 1929. xxvi + 222 pp. 15 X 23 cm. Price, $10.00.

The appearance of this volume in Friend's series on Inorganic Chemistry is welcomed by the increasing number of chemists who have become interested in the elements with which it deals. One hundred and twenty-six pages of the volume are devoted to the chemistry of vanadium and its compounds, thirty-seven to niobium (columbium), and thirty-five to tantalum. As this series is already well known, it is only necessary to say that the volume has been prepared with the same care and in the same style as the previous volumes of the series. Since it deals with three elements which have become increasingly important from the technical standpoint, its appearance at this time is of especial interest. The thoroughness with which the subject matter is treated, together with the large number of references to original articles, should make this book a most excellent basis for students interested in the study of these elements. Industrial chemists who find it necessary or desirable to become more fully acquainted with the chemistry of these elements will find in this volume a most excellent source of information. The book will make a valuable addition to any library on Inorganic Chemistry.

C. W. BALKE

Cours de chimie à l'usage des candidats à l'école des hautes études commerciales et aux instituts de chimie. (A Course in Chemistry for Admission to Business and Technical Schools.) By JEAN ISABEY. Gauthier-Villars et Cie., 55 Quai des Grands-Augustins, Paris, France, 1930. iv + 395 pp. Illustrated. 16.5 X 25 cm. Price, 70 fr.

This is a brief manual or crammer's guide to elementary general and organic chemistry, intended for students reading for the entrance examinations of certain special schools. The selection of topics is guided by the examination syllabus, so that the author feels apologetic for discussing the oxides of nitrogen, which are not on his little list. He has not, however, gone so far as to mention chromium, manganese, cobalt, nickel, cadmium, antimony or bismuth except in alloys, so that the prospective reader need not fear many excursions into useless byways.

In the periodic table used the symbol and atomic weight of radon are incorrect and the "rounded atomic weights include 126 for Te, 127 for I, 240 for U and many other peculiar values. The degree of dissociation of normal solutions of several strong acids is stated to be 93% without further explanation or discussion. It is to be hoped that the book fulfils its primary purpose. It can hardly be recommended to a wider circle.

NORRIS F. HALL

The Beginnings of Chemistry. A Story Book of Science for Young People. By HARRIETT BLAINE BEALE. Illustrations by J. Edmund Woods. Coward-McCann, Inc., 425 Fourth Avenue, New York, 1929. ix + 243 pp. 13 X 19 cm. Price, $2.50.

The author is a lady of outstanding social distinction and charm. Her literary craftmanship is competent and good. She has written many books and her "Stories from the Old Testament" have found constant favor for a score of years. Now the portal of chemistry, the popular exposition of the very beginning of the subject, is so unsatisfactory that we look with eagerness to every new essay in this field. Surely, anyone who can succeed in making Leviticus for the Little Ones or Deuteronomy for Débutantes attractive—although probably under other titles—deserves our earnest attention. The trouble we have in making chemistry a cultural study gives us abundant reason to look diligently for a better approach than we have.

We cannot say that Mrs. Beale has succeeded. Experiments are not recommended to the young readers, which may be of comfort to parents, for children should not play with fire. But the quest of the childish mind to learn what things are made of can hardly be satisfied in a manner to encourage further curiosity when we make the revelation that things are composed of elements. Curiosity is likely to stop right there. The words used in the book are simple but the grasp of the subject is not. Errors are to be found, but more of them would gladly be forgiven if only the approach were made more alluring; in substance rather than in form.

Perhaps some day a popular author will take a leaf from the book of the late Egerton Grey, published by Heffer and Sons, Cambridge, England, and use his little box of tricks. Grey provided weak solutions of reagents which are dropped upon microscope slides, then drawn together by a thin glass rod and the reactions observed through a cheap magnifying glass. That gives the pupil a chance to see something happen. Such a book might expound each reaction and then lure the curiosity of the pupil to the observation of other phenomena, that he sees taking place all around, on every hand. We think this might provide a better start.

ELLWOOD HENDRICK

Cours de chimie-physique. (A Course in Physical Chemistry.) Vol. I. By L. GAY, Professor of Physical Chemistry of the Faculty of Sciences of Montpellier. Preface by G. URBAIN. Librairie Scientifique Hermann et Cie., 6, Rue de la Sorbonne, Paris, France, 1930. xii + 705 pp. Illustrated. 16 × 25 cm. Price, 85 fr.

For some years students at French universities and technical schools have had to depend chiefly on translations of foreign textbooks of physical chemistry. It is hoped that this completely French text may take their place. The plan of the work includes three volumes and the large size of this first volume shows that an extensive treatise is planned. This is the more striking when one sees how narrowly the field treated has been restricted. The author is greatly concerned that physico-chemical questions be treated with rigor and precision, and thus "turns and returns his subjects in every direction, tracing out and finally banishing every ambiguity." Such a method, however, is applicable only to the best-tested and most "classical" part of modern physical chemistry, so that no attempt is to be made, in any of the three volumes projected, to treat atomic and molecular structure, radioactivity or the classification of the elements.

We are left with the following scheme: Volume I, Part I, General Thermodynamics; Part II, The Crystalline and Dilute Gaseous States; Part III, Osmosis and the Phase Rule; Part IV, The Pure Substance; Volume II, Binary and Ternary Mixtures, Chemical Equilibria, Solubility of Solids in Liquids, Alloys, Dilute Solutions—Volume III, Electricity and Magnetism, Capillarity, Colloids, Chemical Kinetics, Radiant Energy, Photochemistry.

The thermodynamical part will not fail to surprise the American-trained reader. After sixteen pages devoted to systems of units (of which more later) the second chapter treats the purely physical relations of work, force, pressure, potential, complete and partial differentiation, etc. Conservation of energy as a purely mechanical principle is followed by Thermometry and Calorimetry, with a misleading diagram to illustrate the calibration of thermometers at the boiling point of a liquid, and with no mention of adiabatic calorimetry. The Principle of the Equivalence of Heat and Work is followed by a brief chapter on thermochemistry, which is intended merely to introduce the Carriot–Clausius Principle. This is elaborated in the classical manner. After the fundamental thermodynamic quantities have been defined and used at length, Entropy, and the two thermodynamic potentials often called "free energy" are mentioned, discussed in a few pages and dismissed with the remark that "their correct application is a delicate matter, their experimental determination difficult," and that "one can easily do without them in studying physical chemistry." They are never again mentioned.

The chapters on the kinetic theory of gases and the crystalline state are followed by one on the specific heat of solids from which one might gather that the determination of approximate atomic weights through the rule of Dulong and Petit was a matter of great importance today. A diagram of the variation of specific heat with temperature is given, but the explanation of the form of the curves, and of the failure of the equipartition theorem is deferred to Volume IV. In the part which follows we find a leading place assigned to osmotic pressure, which is used (since the method of Gibbs has been discarded) in the development of the phase rule. The last part deals with vaporization, sublimation, fusion, equation of state, Brownian movement, crystallization, allotropy. The allotropy of phosphorus is discussed with reference to Jolibois' experiments only, and there is no mention of the problem of black phosphorus. One gathers that the "red phosphorus" formed at 260° is a chemical individual. "Violet" or metallic phosphorus is not discussed. Thirty well-planned problems complete the text. There are no references to the original literature, which must diminish the value of the book as a work of reference. The general atmosphere of the book is one of classical severity and restraint, and no pains have been spared to drive home the important points. The lack of experimental material is perhaps responsible for a certain impression of dryness which the reviewer feels. Where experimental data are used their source is not stated, and the values chosen (e. g., for atomic weights) are not always those currently accepted. The guiding interest seems to have been physical rather than chemical. The reviewer was interested to learn that since **1926** the M. T. S. (mètre, tonne-masse, seconde) system of units has been the legal one in France, including the *sthène* (force giving to a metric ton an acceleration of 1 meter-second), (= 1000 *newtons*), the kilojoule and the *pièze* (1 sthène-meter^{-2}).

NORRIS F. HALL

Röntgenographie der Metalle und ihrer Legierungen. (X-Ray Analysis of Metals and Their Alloys.) By M. C. NEUBURGER, Wien. Ferdinand Enke, Verlag, Stuttgart, Germany, 1929. viii + 278 pp. 66 figs. 16.5 × 25 cm. Price, RM. 25.

This book is a companion volume of the author's "Rontgenographie des Eisens und seiner Legierungen" which appeared last year. In the present volume the author confines himself therefore to the crystal structures of the non-ferrous metals and alloys.

So abundant has been the recent publication of crystal structure data and so widely scattered the places of publication, that one is frequently at a loss to find, without ceaseless searching of the journals, the information which he may want. There is a real need for the compilation and critical analysis of existing crystal structure data, and this the present author has done most admirably in the more limited field of metals and alloys.

After an introduction dealing with the present theory of solid solution in metals (Mischkristalle), the author takes up in each succeeding section first, the crystal structure of each pure metal and then the structure of the alloys of that metal. Where various experimenters disagree, the conflicting data are presented and discussed and the result which seems most probable is stated. Throughout the book the additive relation of Vegard in the case of solid solutions is strongly stressed.

There are given many complete tables of data from the original papers and a large number of cuts of the original powder photographs. An alphabetical index of lattice constants for the metals and their compounds is given at the back of the book and also a full bibliography.

On the whole, this book should prove a very valuable work of reference to anyone interested in this field.

WILLIAM P. JESSE

Handbuch der biologischen Arbeitsmethoden. (Handbook of Biological Methods.) Edited by Professor Dr. EMIL ABDERHALDEN. Section III. Physicochemical Methods. Part B, No. 5. Methoden der Kolloidforschung. (Methods of Investigating Colloids.) Methoden der Viscosimetrie kolloider Losungen. (Viscosimetric Methods for Colloidal Solutions.) By RUDOLF KÖHLER, Leipzig. Methoden zur Bestimmung des kolloid-osmotischen Druckes in biologischen Flüssigkeiten. (Methods for Determining Osmotic Pressure in Biological Fluids.) By MARIE WRESCHNER, Berlin-Dahlem. Methoden zur Bestimmung der elektrischen Struktur kolloider Stoffe, insbesondere der Biokolloide. (Methods for Determining Electrical Structure of Colloids, Particularly of Biocolloids.) By REINHOLD FÜRTH, Prague. Urban and Schwarzenberg, Friedrichstrasse 105B, Berlin N 24, Germany, 1929. xx + 155 pp. 87 figs. 17.5 X 25.5 cm. Price, RM. 9.

Biologists are becoming more curious about viscosity and since many of us have not appreciated that Poiseuille's law is not applicable without modification to protein and to colloidal solutions, Kohler's review comes at an opportune time. He describes methods applicable to protein solutions and gives equations from which true viscosity can be calculated. The paper is devoted principally to work in Wo. Ostwald's laboratory. Perhaps too little attention is paid to the work of Hess and of Couette.

The paper on osmotic pressure contains an excellent summary of the literature and brief descriptions with illustrations of osmometers used by Biltz, Donnan, Sorensen and Krogh, The oncometer used by Schade is described without comment although Krogh and others do not accept Schade's assumption that the osmotic pressure of crystalloids and the imbibition pressure of colloid sols are different phenomena. Schade has coined the phrase "oncotic" to emphasize the distinction. Krogh points out that the experiments of Sorensen, Loeb and Svedberg leave no room for doubt concerning the essential identity of the processes resulting in osmotic pressure of colloids as well as of crystalloids.

Fiirth is an authority on the subject he discusses. The title is rather obscure, for the paper is devoted to methods of measuring (1) potential differences in microscopic dimensions, (2) electrical layers on sol particles by cataphoresis, etc., **(3)** degree of dispersion and diffusion coefficients and (4) dielectric constants.

These three papers conclude the volume on methods of investigating colloids and a subject index of the entire volume is included. Abderhalden adds the comment that observations on the colloidal state frequently employ models so far removed from the living organism that it is difficult to appraise their value to the biologist. Colloid chemistry continues in a state of flux and further developments will soon require an expansion of this volume.

D. B. DILL

Ergebnisse der Agrikulturchemie. Vol. I. (Results of Agricultural Chemical Research.) Edited by Dr. F. HONCAMP, Professor at the Agricultural College and Director of the Agricultural Experiment Station at Rostock. Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1929. vii + 281 pp. 38 figs. 15.5 × 23 cm. Price, unbound, M. 17; bound, M. 18.

The first volume of this publication includes a series of papers which deal with the following subjects: Chemistry and Agriculture; The Distribution and Cycle of Iodine in their Significance for Agricultural Soils; Iodine in Plant Nutrition; The Iodine Problem in Animal Nutrition; The Associative Action of Potassium and Sodium in Plant Growth; Soil Cultivation and Fertilization; Chemical and Biological Aims of Modern Fertilization Methods; The Laws Governing the Digestion of Proteins; Discoveries and Practical Considerations Relating to Phosphorus Investigations in Soils; The Lime Reserves in Our (German) Soils; The Determination of the Absorptive Powers of Soils by the Newer Methods; Electrodialysis and the Problem of Soil Acidity Due to Minerals; The Measurement of the Soil Reaction, Conditions Influencing Changes in Reaction, and Biological Appraisal in Soil Management; Discoveries on the Estimation of Lime Needs and the Effects of the Absorptive Powers of Agricultural Soils.

Two or three of these papers deal with fundamental aspects of plant physiology. The balance of them are concerned with subjects and results that, in the reviewer's opinion, add very little that is new to our knowledge. One gets the impression as he reads these papers that at least some circles of agricultural chemists find it difficult to break away from the shackles which have bound the workers in the field known as agricultural chemistry, and from the conservative habits in investigation and thought which have characterized the past generation of agricultural scientists.

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